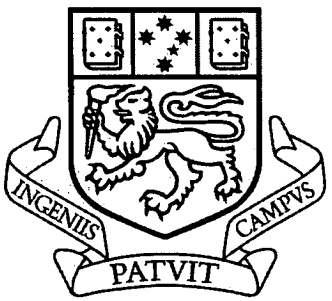
THE EFFECT OF WOOD EXTRACTIVE COMPOSITION ON PITCH DEPOSITION



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for the Degree of

Master of Science.

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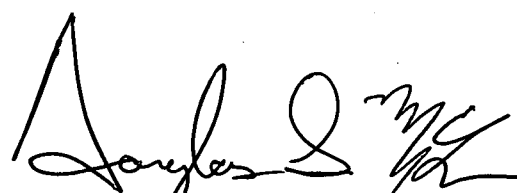

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ABSTRACT

A study of the effects that wood extractive composition has on pitch deposition was conducted using model solutions comprised of a resin acid, fatty acid and triglyceride. The deposition behaviour was investigated under various conditions of pH and temperature.

Statistical pitch deposition models were developed through the use of general multiple linear regression analysis techniques to relate total pitch deposited to the interaction of the various components present in the pitch before deposition. These statistical models were used to predict suitable control strategies for various pH and temperature conditions.

Three of the classes of chemical compounds found in wet end and wood extractive chemistry were investigated in this study. The results and deposition models developed help to explain why strategies to control wood pitch deposition have and/or have not worked.

Mechanisms of the interaction between components are proposed, based on evidence from this work and corroboration of papers from the literature.

The techniques reported in this thesis form a framework under which more complex and in depth wood pitch deposition studies could be conducted.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

GLOSSARY

- 2D –two-dimensional
- 3D –three-dimensional
- 4D –four-dimensional
- β_i – regression coefficient
- BSA – N,O-bis(trimethylsilyl)-acetamide
- BSTFA – N,O-bis(trimethylsilyl)trifluoroacetamide
- DOG – 1,3-dipalmitoyl-2-oleoyl-glycerol
- *FAP* – fatty acid present prior to deposition (oleic acid)
- FID – flame ionisation detector
- F-ratio – the ratio between treatment mean square and error mean square (the larger the F-ratio the greater the significance of its corresponding model)
- GC – gas chromatography
- *GLP* – triglyceride present prior to deposition (triolein)
- pKa – negative of the log of the acid ionisation constant (lower the value the greater the ionisation of the acid).
- PVT-HTGC-FID – programmed injection temperature on-column high temperature gas chromatography with a flame ionisation detector
- R^2 – is the coefficient of determination ($0 \leq R^2 \leq 1$, where higher values signify that the associated model describes a large portion of the variation)
- R_A^2 – is the adjusted coefficient of determination that compares the variance estimates both with and without explanatory variables ($0 \leq R_A^2 \leq 1$, where higher values signify that the associated model describes a large portion of the variation)($R_A^2 \leq R^2$)
- *RAP* – resin acid present prior to deposition (abietic acid)
- rpm – revolutions per minute
- SPLOM – scatter plot matrix
- *t*-BME – tertiary butyl methyl ether
- TCMS – trimethylchlorosilane
- *TPD* – total pitch deposited

1. INTRODUCTION

The following chapter is meant to provide an overview of the topics explored within the thesis, by introducing key terms and issues and ultimately the aim of this work.

1.1 Wood Resin

Wood resin is a broad term that encompasses an extraordinarily large number of individual chemical compounds found in trees[1]. These compounds although not part of the structure of the tree, aid the tree in a number of its biological needs. These biological needs include nutritional[2], insecticidal, fungicidal and microbicidal[3, 4] functions important to the survival of the tree[1]. Chemically speaking wood pitch is a combination of lipophilic, dissolving in fat(s), and hydrophilic, dissolving in water, compounds that can be extracted from a tree or plant. Since wood pitch can be extracted from trees it is often referred to as wood extractives, extractive material or simply as extractives. Although wood extractives are technically the lipophilic, water insoluble, and hydrophilic, water soluble, extracts from the tree the term "extractive" in this context is usually only representative of the lipophilic part[5]. This lipophilic portion of the wood extractives also encompasses the amphiphilic portion, which are components that have both a polar and a non-polar centre. These lipophilic wood extractives are often referred to as resinous extracts, or resins.

The function of a particular extractive component usually dictates its location within the structure of the tree[6]. The location[7] and quantity of the extractives varies genetically[8], geo-ecologically, seasonally[9] and morphologically[6] from tree to tree.

Wood resin can exist in a variety of physio-chemical forms during wood processing[10]. When wood resin combines with other material to form a deposit this substance is referred to as "pitch". "Encapsulated pitch" is a term used to describe resin trapped within the cellular structure of wood fibre. "Attached pitch" is a term to describe resin attached to the outside of wood fibre. "Soluble pitch" is a term used to describe resin in solution, usually water. "Colloidal pitch"[11] is a term used to describe a mixture of resin components which are arranged in a structure that allows them to remain homogeneous with the solvent they are in (i.e. water). This colloidal structure is usually referred to as a pitch particle and has an average size close to a micron in diameter. "Agglomerated pitch" is a composite of resin molecules which

is neither in the "colloidal" nor the "attached" form, "agglomerated pitch" usually comprises molecules larger than "colloidal pitch". "Deposited pitch" is a term used to describe "agglomerated pitch" that has ceased being in solution and has deposited on to a given surface. Under the proper kinetic conditions (i.e. temperature, pH, concentration and time) pitch can shift from one form to another. The papermaking chemist can, with some difficulty, deal with many of these forms of pitch, the most challenging being "deposited pitch".

1.2 The problems of wood pitch deposition – past and present

The deposition of wood pitch onto the surfaces of papermaking machinery has been a problem for many years. The chemical pulping of wood, removal of fibre from the tree, was introduced in the mid nineteenth century. These innovations allowed for whiter and stronger sheets by separating, and removing, the lignin and the resinous material from the wood cellulose. By the end of the nineteenth century the use of chemical pulping was widespread, and with it came the widespread problem of wood pitch deposition. In 1917 Johnsen[12] wrote, "These so called 'pitch troubles' are in fact so common in the paper mills that the necessity of finding a method for their elimination by removing from the pulp the resinous substances is one of the great problems in the manufacture of sulphite pulp at the present time." This wood pitch deposition problem continued for many years; in 1924 Wells[13] wrote, "Among the most elusive difficulties met with by papermakers are those due to pitch." Shortly thereafter methods of washing the extractives out of the pulp and into the effluent were found and implemented. On occasion however the problems would still affect the pulp and paper production and as a result the need for scientific research onto the problem increased. In 1936 Kress and Moss[14] wrote, "The extensive literature on pitch abounds with conflicting theories on the causes of and possible methods for eliminating pitch troubles, but none of these theories adequately explains why pitch troubles occur or how to prevent them." Due to the analytical techniques of the time almost every extractive component was blamed for the deposition of pitch, this was summarised in a review by Vincent[15] in 1957.

The enthusiasm for environmental improvements in the pulp and paper industry grew throughout the 1970s and 1980s. The two areas of environmental improvement focused on the increased use of post-consumer recycled fibre and the reduction in the toxicity of effluent waters. Both of these environmental improvements increased the

difficulties associated with wood pitch deposition. The hydrophobic nature of the contaminants in recycled fibre exacerbated the formation of wood pitch deposits and led to Hassler[16] making the following statement in 1988, "The formation of deposits of resinous substances (pitch, stickies) in paper machine systems presents a serious problem for the paper industry and has been the subject of many papers published over several decades. Despite considerable effort, it has not been possible to clearly elucidate the mechanisms of deposit formation because of the extreme complexity of these systems." The toxic nature of wood resin was clearly highlighted for resin acids by McFarlane and Clark[17] in 1988 and for fatty acids by Leach and Thakore[18] in 1973. This identified toxicity required a change in "wash it out, flush it down" approach that had been used in the control of wood pitch depositions. During the 1970s and 1980s methods for the control of pitch deposition, rather than the redirections of resinous extractives to the effluent, gained in popular use.

This movement towards pitch deposition control has gained more momentum in the 1990s with the industrial/environmental trend towards the reduction in total fresh water, and consequently effluent, used in the papermaking process. The need for even better understanding of pitch deposition under this water reduction, or mill closure, period was summarised by Thornton[19] in 1993 when he wrote, "Improved understanding of the basic chemical interactions taking place in the wet-end of the papermachine is necessary when considering new ways in further closing mill water systems. In order to better understand the wet-end chemistry in the production of wood-containing paper, the dissolved and colloidal substances released from wood must be better characterized."

The problem of wood pitch deposition however still exists today. A recent (i.e. 2003) publication by Bergelin and Holmbom [20] stated, "Moreover, so-called pitch problems, in the form of deposition of wood resin on the surfaces of process equipment, are common..."

The Norske Skog Paper Mills (Australia) Limited Albury (New South Wales) mill has had problems with pitch deposition since the start-up of its papermachine in 1981. The process chemists have tried many different control strategies over the past 22 years[21-23]. An outbreak of pitch deposition in 1995 prompted a detailed study into the factors affecting pitch deposition at the mill[23]. The fibre source at Albury is a

combination of thermo mechanical pulp (TMP) made from *Pinus radiata* and recycled fibre (RCF). In examining these fibre sources Richardson *et al*[23] found that the deposits were a function of the seasonal variation within the triglycerides and resin acids of the *Pinus radiata*, though predominately the high resin acid content. pH and its affect on the solubility of resin acids was theorised as a potential explanation of the pitch deposition. Various control strategies were explored and an effective method was chosen, where the extractives were removed from the system using chemicals in a dissolved air flotation (DAF) unit. A subsequent increase in the paper's RCF content reduced the efficiency of this control strategy. As a result a further study was conducted by Richardson *et al*[22] in order to investigate new means of chemically reducing pitch deposition. It was found that the higher divalent calcium cation (i.e. Ca^{2+}) content, from the RCF, favoured the chemical fixation of the extractives to the wood fibres. In an effort to better understand the pitch deposition problems at Albury, Stack *et al*[24] examined the issue through the use of model extractive compounds in an effort to reduce the amount of variables present in using industrial wood extractives. Their findings supported the observed seasonal pitch deposition outbreaks through the viscosity of the seasonally varying components. The change in system pH from acid to near neutral conditions, at the Albury mill, in late 2001 increased pitch deposition and prompted Richardson *et al*[25] to re-examine pitch fixative chemistries and their performances under neutral pH conditions.

1.3 Aims of thesis

There are two primary aims to this study. The first aim is to determine whether or not deposition interactions exist between model pitch extractive components under modern papermaking conditions. The second aim is to describe and theorise the nature of these potential interactions in a variety of temperature and pH conditions. These aims were explored using laboratory deposition studies and rigorous statistical analysis of data collected from this, and previous studies. This study was funded by Norske-Skog Paper Mills (Australia) Limited and the Pulp and Paper research group of the University of Tasmania's School of Chemistry in hope of better understanding the nature of pitch deposition and its potential reduction and control.

2. LITERATURE REVIEW

This chapter has been included to review research that has been conducted in areas similar to work conducted in this thesis in order to establish the context and relevancy of this work.

2.1 Wood resin composition

Wood extractives are found throughout the tree. The parenchyma and secretory tissue (i.e. resin canals) are where the majority of extractive compounds can be found[26]

Although the composition of wood extractives was traditionally classed by their extraction techniques[27], they are now classed by differences in chemical structures, as detailed in Table 2.1.

Table 2.1. The five classes of lipophilic components.

Class	Lipophilic component
1	Terpenoids
2	Phenolic compounds
3	Fatty acids and fatty acid esters
4	Waxes
5	Fatty alcohols and sterols

Mono-, di- and sesquiterpenoids are generally volatile and give the tree its distinctive odour. These compounds are the primary components of turpentine and can constitute up to thirty percent of the total extractives from a tree[28], with even higher percentages found in the pine needles[29]. Some examples of these volatile terpenoids are shown in Figure 2.1.

Tricyclic diterpenoids (i.e. resin acids) are generally divided into two groups, those similar to abietic acid and those similar to pimaric acid[30]. The eight common resin acids are shown in Figure 2.2. The abietic-type acids possess an isopropyl or isopropylidene group at the thirteenth carbon (Fig. 2.2) where as the pimaric-type acids have a methyl and vinyl group at the thirteenth carbon[31]. Although dehydroabietic acid shares the criteria of the abietic-type acids the author has placed

it in a separate category due to its aromatic ring[32]. The main function of resin acids is to seal the trees wounds from fungal and bacterial attacks[33] as resin acids are toxic to most fungi and bacteria[34].

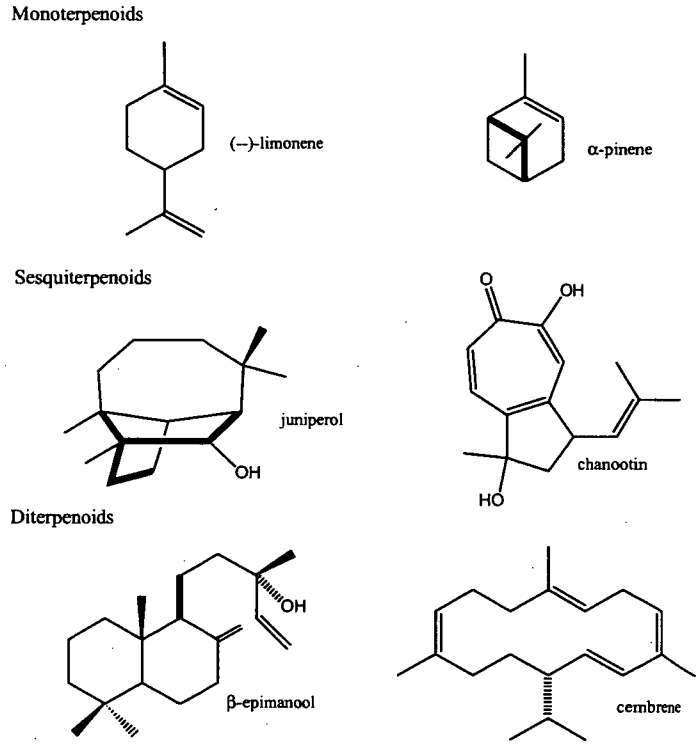


Figure 2.1. Examples of terpenoids.

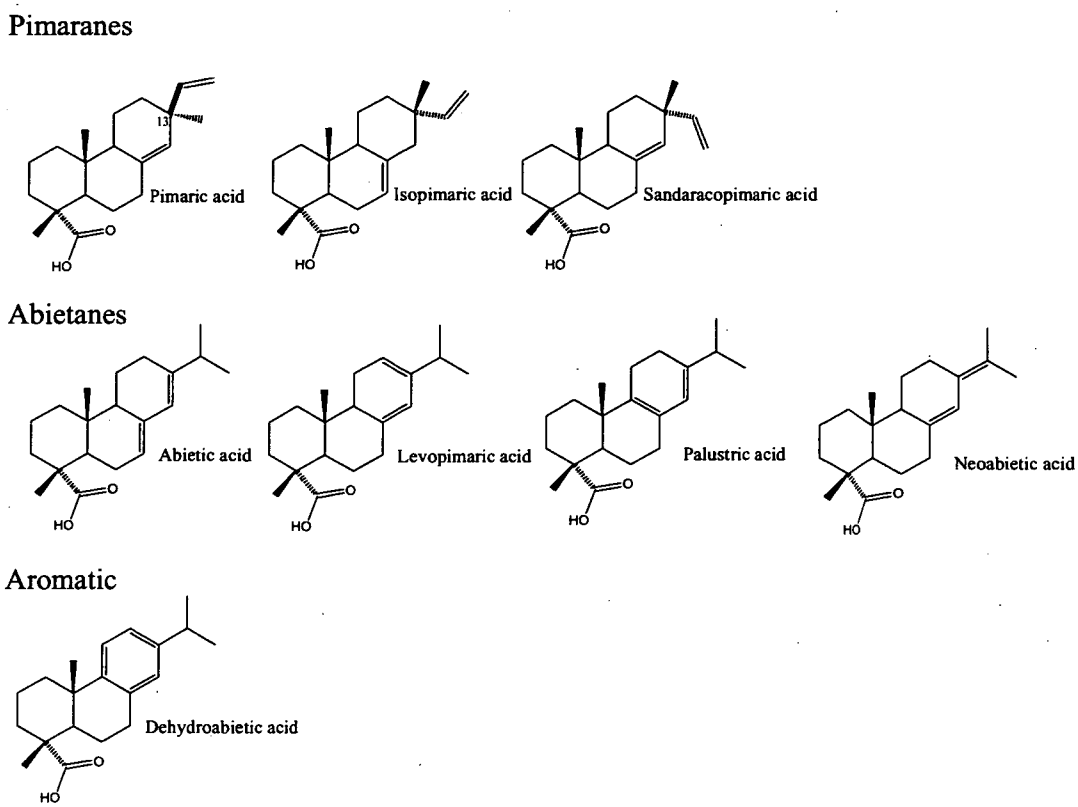


Figure 2.2. Examples of resin acids (i.e. tricyclic diterpenoids).

Sterols are strongly hydrophobic[1] and represent a large portion of the extractives that remain in some hardwood pulps[20]. Two examples of these sterols are shown in Figure 2.3.

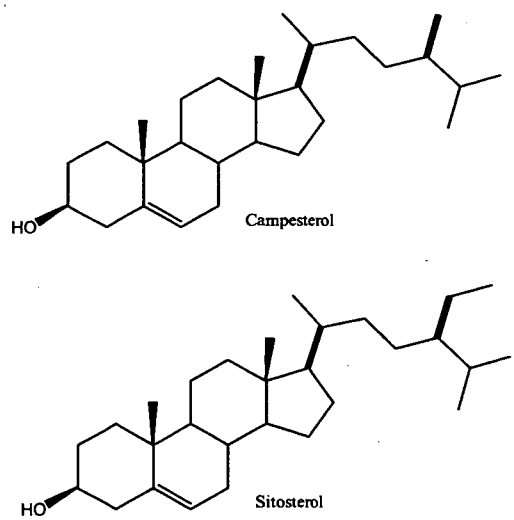


Figure 2.3. Examples of sterols.

Phenolic compounds are founds throughout the tree, lignans in particular can represent up to twenty four percent of the extractive content of Norway spruce knots[35]. Tannins are quite common in eucalypts[36]. These and other phenolic compounds are shown in Figure 2.4.

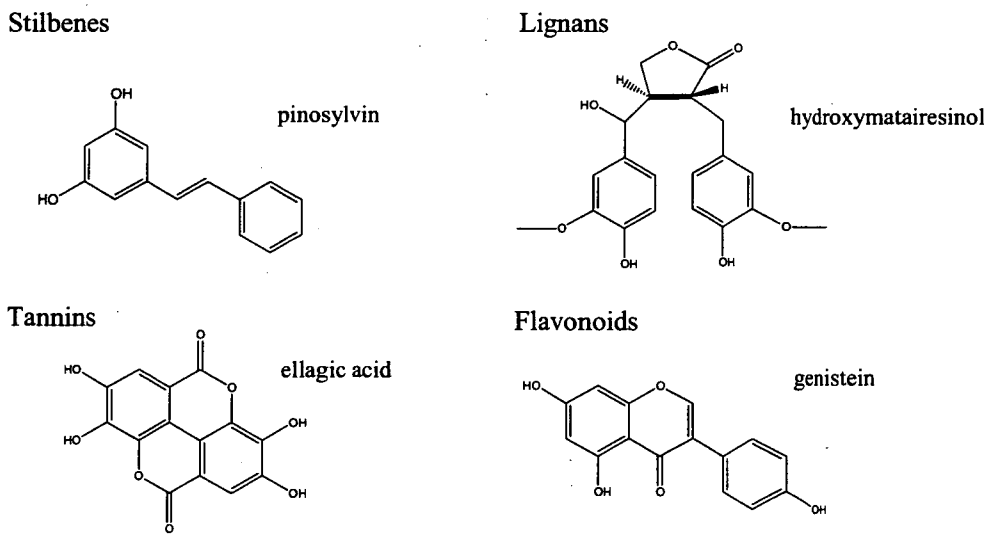


Figure 2.4. Examples of other phenolic compounds (i.e. aromatics).

More than thirty saturated and unsaturated[1] fatty acids, of chain lengths typically between twelve and twenty-four carbons[2], are found in wood extractives. These fatty acids are often stored as triglycerides (i.e. fats) within the tree. A few fatty acids and triglycerides are presented in Figure 2.5.

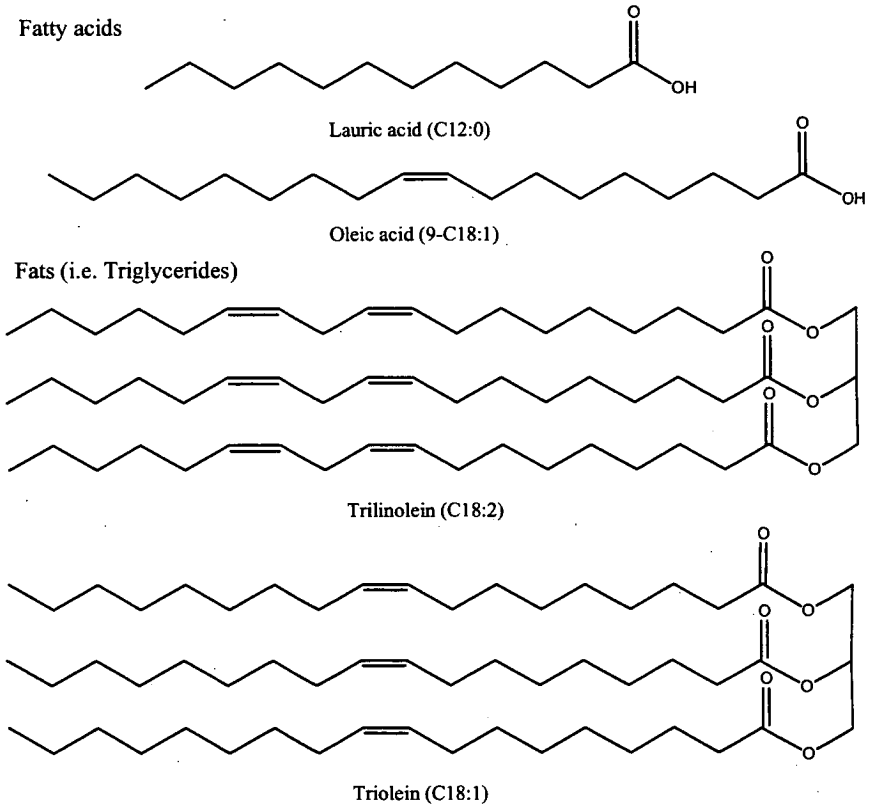


Figure 2.5. Examples of fatty acids and triglycerides.

Waxes are primarily the esters of sterols and fatty acids, though longer chained (i.e. >20 carbons) free alcohols of fatty acids are also considered waxes[1]. Some examples of these waxes are shown in Figure 2.6.

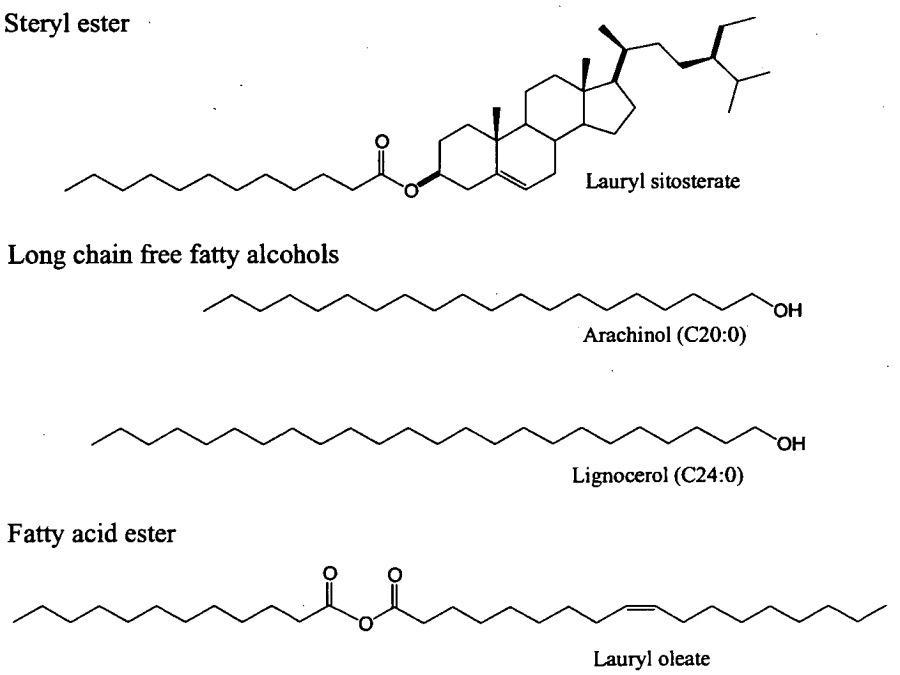


Figure 2.6. Examples of waxes.

Wood resin analysis

It wasn't until the start of paper sizing (wet ink hold out through the use of wood oleoresins) in the early 1800s, that the study of the chemical nature of wood extractives started. The understanding of wood pitch deposition and the reduction, or controlling, of this deposition has advanced alongside wood extractive analytical techniques. One of the earlier breakthroughs came in 1891 when Twitchell[37] demonstrated a method to separate the resin acids from the fatty acids through esterification of the fatty acids and subsequent evaporatory separation of the two components. By the 1930s organic separation techniques for almost all components of wood extractives had been developed, though analysis was time consuming, tedious and usually conducted gravimetrically[38]. Due to these time consuming analytical techniques most of the pitch components were not separated from one another during experimentation. As a result the deposition research of the time was usually reported in mass of pitch deposited.

A wide variety of techniques used for the separation and identification of various wood extractives are now available. These analytical techniques include; high-performance liquid chromatography (HPLC)[39], size-exclusion chromatography (SEC)[40], high performance size exclusion chromatography (HPSEC)[41], infrared spectroscopy (IR)[42], super critical fluid chromatography (SFC)[43], thin layer chromatography (TLC)[44], pyrolysis gas chromatography (Py-GC)[45]. Advances in GC techniques continue to develop. Today commonly used analytical methods include programmed injection temperature on-column high temperature gas chromatography with a flame ionisation detector (PVT-HTGC-FID)[46], gas chromatography mass spectroscopy (GC-MS)[47] and visible ultraviolet light measurements (UV-vis)[48].

Wood resin analysis by GC

The major advantage of the short column PVT-HTGC-FID techniques is the ability to analyse a wide variety of extractive compounds in one step. GC analysis methods of Örså and Holmbom[46], Thurbide and Hughes[49], Wallis and Wearne[50], and Corin *et al*[51] have been used for GC analysis of fatty acids, resin acids and triglycerides. Summaries of their GC columns and carrier gases are reported in Table 2.2.

Table 2.2. GC columns and carrier gases from a variety of published works.

	Örså and Holmbom[46]	Thurbide and Hughes[49]	Wallis and Wearne[50]	Corin et al[51]
Column	DB-1	DB-5	DB-1	HP1
Column length (metres)	5	5	10	25
Column i.d. (mm)	0.53	0.53	0.53	0.2
Column stationary phase film thickness (μm)	0.15	0.15	0.15	0.33
Carrier gas	Hydrogen 20 mL/min	Helium 5 mL/min	Helium 5 mL/min	

t-BME and DCM (dichloromethane) have been used as the solvent for liquid-liquid extraction as shown in Table 2.3.

Table 2.3. Liquid-liquid extraction techniques from a variety of published works.

	Örså and Holmbom[46]	Wallis and Wearne[50]	Corin *et al*[51]
Liquid-Liquid Extraction	*t*-BME	DCM	*t*-BME

Extractive composition of Pinus radiata

The experimental work of this project, though conducted with model compounds, was based on the composition of *Pinus radiata*. McDonald and Porter[52] analysed the acetone extracts of green *Pinus radiata* logs by GC, their results are shown in Table 2.4.

Table 2.4. Extractive classes from *Pinus radiata*[52].

Class of analyte	% of total extractives
Resin acids	58.8
Fatty acids	11.2
Esters as triolein	7.6
Phenolics	5.2
Unsaponifiables (i.e. sterols)	16.3
Essential oils	0.8

McDonald and Porter[52] went on to analyse *Pinus radiata* tall oil, also by GC. Their results are shown in Table 2.5. The compositions of fatty acids listed in Table 2.5 are a combination of the free fatty acids and the hydrolysed triglycerides.

Table 2.5. Fatty acid and resin acid extractives from *Pinus radiata* tall oil[52].

Analyte	% of total composition
C16:0	0.7
C16:1	1.2
C17 Br (anteiso)	0.2
C18:0	0.8
C18:1 (oleic)	4.3
C18:2 (9,12)(linoleic)	1.1
C18:3 (9,12,15)(linolenic)	17.1
C20:1	6.6
C20:2 (11,14)	2.1
C20:3 (5,11,14)	n.d.
C22:0	2.9
pimaric	4.5
sandaracopimaric	4.2
palustric/levopimaric	0.7
isopimaric	5.9
abietic	39.9
neoabietic	7.9
Total fatty acids	36.9
Total resin acids	63.1

Suckling *et al*[53] examined *Pinus radiata* extractives by HPLC, the results of which are shown in Table 2.6. Although Suckling *et al*[53] detected sterols, the results were not reported quantitatively.

Table 2.6. Extractives from *Pinus radiata* via HPLC[53].

Analyte	% of total extractive
dehydroabietic acid	5.7
other resin acids	21.8
linoleic acid (C18:2)	2.9
palmitic and oleic acids (C18:1)	4.3
triglycerides	35.0

Wallis and Wearne[41] examined DCM extractives of fresh *Pinus radiata* wood chips by HPSEC and GC-MS. Their results are shown in Tables 2.7 and 2.8.

Table 2.7. Extractives from *Pinus radiata* via HPSEC[41].

Analyte	% of total extractive
triglycerides	21.8
steryl esters	5.2
fatty acids / sterols	0.9
resin acids	72.0

Table 2.8. Extractives from *Pinus radiata* via GC-MS[41].

Analyte	% of total extractive
resin acids	96.0
fatty acids	3.2
sterols	0.8

2.2 Wood pitch deposition

Wood pitch deposition is normally explained in terms of colloidal pitch instability, although it is uncertain as to how these chemically homogenous colloidal particles are formed. Coagulation of these colloidal particles and their subsequent precipitation, or deposition, can be explained by colloidal instability caused by temperature, pH, metal ions, electrolytes, charge, surfaces, shear forces and viscosity.

Back[54] explained that with increases in temperature resin and fatty acids become more soluble (i.e. not colloidal). He stated that fatty acid solubility doubles by increasing temperature from 25 to 50°C. Dreisbach and Michalopoulos[55] demonstrated the difficulty in establishing an ideal system temperature as they found that abietic acid deposited least at low temperatures, whereas the deposition potential of fatty acids were at a maximum under the same conditions.

Suckling *et al*[56] showed that the solubility of triglycerides, resin and fatty acids increased with increases in pH. They also showed that it was possible to hydrolyse triglycerides into fatty acids and diglycerides at pHs above 9. Kanicky and Shan[57] showed oleic acid (C18:1 fatty acid) to have a pKa value of 9.85, where as Nyrén and Back[58] showed abietic acid (a resin acid) to have a pKa of 6.4. Nylund *et al*[59] showed that the colloidal size of pitch particles increases with increases in pH. There has been difficulty in establishing an ideal system pH, due to the variable depositions at most pHs[55].

Allen[60] showed that metal-soap deposits usually contain multivalent metal ions (i.e. Ca^{2+}, Mg^{2+}, Ba^{2+} or Al^{3+}) from either the wood[61] or the water (i.e. hardness). This deposit can be represented by the following reaction between the anionic soap of the fatty or resin acid and the metal cation:

$$M^{n+} + nSoap^{-} \rightarrow M\ Soap_n \downarrow$$

(Metal cation) (Soap anion) (Metal soap)

Reaction 2.1. [60]

The resulting multivalent metal soap is sticky and insoluble (sodium being the exception), as Allen studied synthesised metal soaps and compared them to the texture of bubble gum. He found that Reaction 2.1 was effectively irreversible even at pH 4. Allen believes that under acidic papermaking conditions (e.g. 5.5) these anionic soaps normally react with free hydrogen ions to form insoluble fatty and resin acids, as shown in Reaction 2.2.

$$Soap^{-} + H^{+} \leftrightarrow H\ Soap \downarrow$$

(Soap anion) (acid) (Fatty or Resin acid)

Reaction 2.2. [60]

Allen used these reactions to explain why metal ions are only found in pitch deposits when there is a rise in pH (i.e. pH shock).

Sundberg *et al*[62] demonstrated that steric stabilisation of the colloidal pitch particles may play a role in reducing pitch deposition as the colloidal particles were fairly stable even at high concentrations (i.e. > 10 mmol/L) of electrolytes.

Trafford[63] indicated that a colloidal system was charge-stabilised in so long as system zeta potential (a measurement of charge) did not exceed +/- 20mV.

Back[64] clearly demonstrated that surfaces affect pitch deposition by analysing the amount of pitch deposited onto a variety of surfaces. His results are summarised in Table 2.9.

Table 2.9. Pitch accumulated of a variety of surfaces[64].

Material	mg of pitch accumulated
Glass	0
Rubber	12
Regenerated cellulose film	19
Aluminium	28
Copper	45
Phospor bronze wire	42
Polytetrafluorethlene	44
Woollen felt	229

Ohtani[65] showed that an activated (+50 Volt) carbon cloth could adsorb 10 to 15 times the amount of extractive material as steel.

Back[64] also showed that shear forces have a significant impact on pitch deposition. The results of this study show that doubling an impeller's rotational speed nearly doubled the pitch deposited. There was however a limit to this proportionality as the impeller he was using had maximum deposition rate at approximately 1000rpm.

Vincent[66] was able to relate pitch tack (i.e. plastic viscosity) to pitch deposition. The viscosity, or stickiness, of pitch has been used by a number of authors to explain pitch deposition[24, 64, 67]. This desire to relate pitch deposition to pitch tackiness, stickiness and viscosity is most likely due to the fact that pitch deposits vary significantly in their tack, viscosity and stickiness.

Laboratory deposition apparatuses

A wide variety of laboratory deposition devices have been used over the years. Early deposition studies[68, 69] made use of device called the "Lampén mill" in which pitch was deposited onto steel ball bearings in an agitated vessel. Kress and Moss [14] and Ståhlberg [70] used a "Valley Beater", also known as a "Hollander beater", which had brass plates that were dragged along the surface of a pulp suspension to collect pitch. Kress and Moss[14] also used a simple propeller mixer to collect pitch. Samuelsen[71] developed a metal mixer that spun inside of a separatory funnel, such that the pitch could then be easily solvent extracted from the propeller after deposition had taken place. Kress and Nethercut[72] used metal screens, to collect pitch, that were placed on a rotary shaft in order to simulate the screening surfaces from within the papermaking process. Gavelin[73] and Ströle and Teves[74] used a flotation process as pitch often collecting in foam on top of chests and storage vessels within the paper mills. Gustafsson *et al*[75] developed a copper vessel with a copper impeller in order to study pitch deposition as papermaking equipment and storage vessels were frequently covered in copper. This copper vessel was modified by Vincent[15] such that it could be placed within a temperature bath; and later modified by Back[64] in order to study the surface selectivity of pitch deposition. Ströle and Teves[74] also used a vibrating mixer to study pitch deposition under shear forces more representative of those found within the papermaking process. Hassler [16] and Welkener et al [76] later used a modified version of this mixer, called the

"Vibromixer". Further improvements on the "Vibromixer" led to the "UCM-deposition rotor" made popular by Blanco *et al*[77] and Otero *et al*[78]. A recent study by Willför *et al*[79] used a laboratory magnetic stirrer to study the fixation of extractives onto fillers. Stack *et al*[24] used polyethylene vessels and polyethylene stir paddles, under conditions of constant shear and temperature, in an effort to reduce pitch deposition induced by the surface of the laboratory equipment (e.g. glass).

2.3 Control, management and elimination of wood pitch deposition.

Many aspects of wood deposition reduction and control are now being investigated. These investigations can be divided into four schools of thought; 1) Pulping operations – through removal of extractives prior to the papermachine. 2) Biological - through treatment of the raw and/or processed fibre. 3) Forestry/Agricultural - through selective, alternative and/or genetically modified fibres as well as harvesting and storage techniques of the wood and/or wood chips. 4) Chemical - through dispersant and/or fixation of colloidal and agglomerate pitch. Traditionally reducing pitch deposition was accomplished through modifying pulping operations, and some of this type of work continues today. All four of these areas will need to continue in order to minimise problems associated with wood pitch deposition. Not included in these four areas is the importance of process stability, namely stable pH, temperature and shear as a shock of any of these three process parameters is likely to lead to pitch deposition[80].

Pulping operations

Washing of the pulp through the use of soft water (i.e. water low in metal ions such as Ca^{2+}), sudden cooling of unwashed pulp and the use of woollen felts have effectively been used to remove pitch from a pulp stream before it reaches the papermachine for many years[12]. Kress and Moss[14] later showed that there was little difference in the hardness of the water and speculated that this was due to the emulsion (i.e. colloidal) stabilising effect of the electrolytes in the harder water. They did however agree with the use of cold water for washing. Örså *et al*[81] demonstrated that more extractives were washed from the pulp with increased pH, in the range of 4.5 to 6.7. Bleaching also plays a significant role in the removal of extractives from pulp[82], as does the pressures under which chips are pulped[83]. Pitch can also be removed though the use of dissolved air flotation (DAF) units[23].

Biological

One of the functions of wood extractives is to protect the tree from biological attacks. There are some living microscopic compounds, which can however breach these natural defence systems. Once a tree is chipped and/or pulped it becomes much easier for the extractive compounds to be broken down by biological means. When a tree lies dead in the wild it begins to rot and decay until the entire tree has become soil. This process can take quite some time and is accomplished through the contribution of many organisms. Some of the fungi involved in this decaying process specifically target the extractives in the tree. The pulp and paper industry has taken advantage of these fungi and has used them to remove extractives from the wood chips as they are stored prior to pulping[39, 84-87].

Extractive components that remain in effluent streams may also be broken down by light[51] and biological means[88-90]. Liss et al [91] compiled a review of the biodegradation of resin acids. The industry has designed activated sludge systems taking advantage of these aerobic bacteria to break down of extractive components prior to discharging the effluent into waterways[92, 93]. Degradation can also be conducted within the papermaking process as the temperatures, pHs and closed (i.e. highly recirculatory) water systems are favourable to certain bacteria[94].

Enzymes that hydrolyse triglycerides into their fatty acids have been used to reduce pitch deposition[95]. The principle of enzymatic hydrolysis is shown in Figure 2.7.

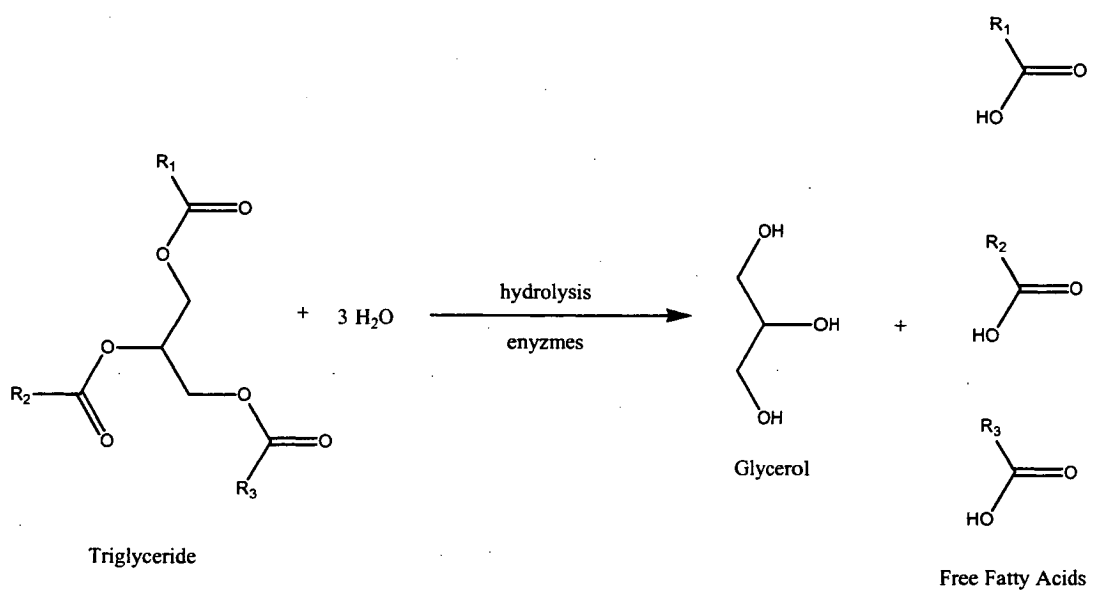


Figure 2.7. Principle of enzymatic hydrolysis of triglycerides[96].

Another approach is to install a biotechnological "kidney" to closed process water systems in order to remove extractives from the system[95]. This area of pitch control has been developing quite rapidly in recent years, and Gutiérrez *et al*[97] has summarised these biotechnological pitch control trends in a review paper.

Forestry/Agricultural

Effective delimbing[29] and debarking[98] are important to the reduction of pitch deposition as the bark and needles contain relatively high proportions of extractives. Extractives vary with the age of a tree[7, 40] and within different sections of the tree[99] with the heartwood of the older trees having the highest resin acid levels. The genetics of a tree (i.e. clonal variation) also have significant influence on the extractive composition and load[8]. The much publicised "pitch season"[100], or the annual period of pitch deposition has been associated with seasonal variation of extractive components within trees[23]. The seasoning, or aging of logs and chips prior to pulping, has been used to dampen these cyclical variations in extractives[63, 101, 102].

Chemical

Enckell[103] believed that pitch deposition was due to colloidal instability and as a result theorised three possibilities by which "rosin suspensions"(i.e. colloidal pitch) could be converted into forms that were not harmful to paper manufacture. The first possibility was through the stabilisation of suspensions by the addition of a "peptonising emulsoid"(i.e. surfactant). The second, was by adsorption of the "rosin suspension" onto a suitable "suspenoid"(e.g. talc, wool, etc.). The third option was to fix the "rosin suspension" to the pulp fibres. Chemical programs are normally evaluated by measuring the amount of pitch deposited, but Garver and Yuan[104] have suggested using the stability of colloidal particles as a measure of chemical program effectiveness.

Colloidal stability can be improved by the addition of dispersants[105, 106]. This improved colloidal stability has been shown to reduce pitch deposition. Improved colloidal stability has also been demonstrated through the use of electrolytes, such as $CaCl_2$[11].

Disrupted colloidal stability through the addition of high surface area hydrophobic fillers, such as talc[107] and bentonite[13], have also been effective in reducing pitch deposition. Minerals, such as heulandite, have been organically cationised in order to increase their effectiveness at reducing pitch deposition[108]. It is believed that these fillers, by adsorption, help to detackify (reduce tackiness) the pitch particles and hence reduce their deposition. Structured proteins[109] and non-ionic polymers[110] have also been added to papermaking waters to promote the detackification, improved stability and reduced deposition of pitch particles.

Fixative chemistries have been used to control pitch deposition for nearly two hundred years, by attaching pitch particles to the pulp fibres. Early fixative applications of alum (Al $K(SO_4)_2 \cdot 12H_2O$) not only reduced pitch deposition[111] but also provided paper with sizing (hydrophobicity for improved printing)[112]. Coagulants such as polyethyleneimine (PEI)[22, 25], poly-dimethyldiallyl-ammonium chloride(DADMAC)[113] and acrylamide copolymers[21] have been effective at reducing pitch deposition through fixation of pitch particles to the pulp fibres. Shetty et al [114] described a likely mechanism of this fixation as the pulp fibre matrix entrapment of pitch particles that were enlarged through coalescence of pitch colloids through the addition of cationic fixatives.

There are a number of chemicals that can have a negative effect on pitch deposition. Defoamers, which are usually oil or silicone based tend to increase pitch deposition as do synthetic sizing agents such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA)[80], the structures of which are shown in Figure 2.8.

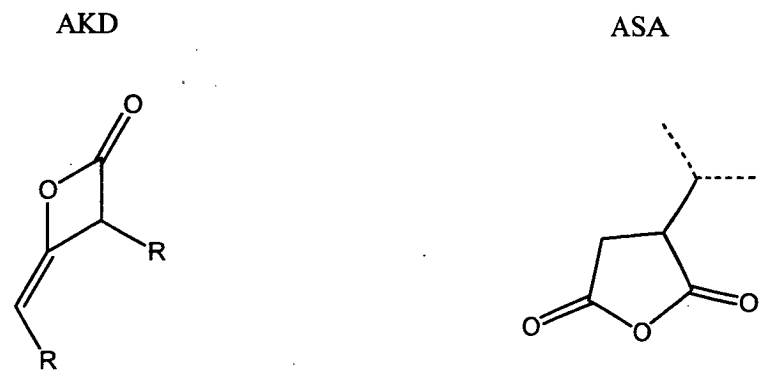


Figure 2.8. Chemical structures of AKD (alkyl ketene dimer) and ASA (alkenyl succinic anhydride).

Nguyen[106] demonstrated that "stickies" interacted with pitch extractives to increase deposition. He described "stickies" as a recycled paper term that refers to the hydrophobic components used in the manufacture of paper products; the term is also used to describe deposits that contain these hydrophobic components. A partial list of these hydrophobic components includes styrene butadiene rubber (SBR), vinyl acrylates, polyisoprene, waxes, tackifying resins and polybutadiene. His work showed that this interaction between hydrophobic components (i.e. pitch and stickies) could be reduced by the addition of low molecular weight, high charge density coagulants.

2.4 The effect of wood extractive composition on deposition

Vincent[15], in 1957, wrote, "In the past, all fractions of pitch have been blamed, but the neutral or non-polar components have been considered particularly as the cause of pitch deposition." These "non-polar" components encompass practically all of the extractive components with the possible exception of flavonoids, tannins and lignans. Vincent summarised much of what was known in regards to pitch deposition in 1957; he utilised earlier summaries by Phillips[38] and Kress and Moss[14].

A large number of researchers of that time believed that the fats (i.e. fatty acids and triglycerides) were the components responsible for pitch deposition[12, 115]. Others more or less supported this theory by saying that the fats played a key role in pitch deposition, through interaction with other components[116, 117]. Tydén[118] made the argument that it was the interaction between the fats and resin acids that caused the pitch deposition and that the fats played the primary role in these interactions. Holmberg[119] believed that the unsaponifiable fraction was dangerous and Ståhlberg[67, 120] believed that the plastic nonpolar fractions caused pitch troubles. These fractions are most likely what are now called waxes and sterols. Richter[121] considered the water-soluble extractives (e.g. carbohydrates and inorganic material) to be significant in pitch deposition. Sieber[122, 123] believed that pitch deposition was a mixture of fatty and resin acids together with their glycerides (i.e. triglycerides) and the unsaponifiable material (i.e. waxes and sterols).

There have been few component dependent, or component interactive, deposition papers published since the Vincent's summary in 1957. Supporting the theories of

Holmberg and Ståhlberg is more recent work by del Río *et al*(1998)[124] and Speranza *et al*(2002)[125]. del Río *et al*[124] also showed that minor amounts of ellagic acid (a tannin) were found in all pitch deposits where *Eucalyptus globulus* was used as a wood source.

Allen(1980)[10] explained an interaction phenomenon now referred to as "pitch seeding" wherein once a pitch deposit has formed more colloidal extractive material will leave solution and precipitate onto the deposit.

Hassler(1988)[16] as well as Dreisbach and Michalopoulos(1989)[55] set out to understand pitch deposition in terms of its response to various pitch-control agents. Inadvertently, these works suggested that interactions between components might be influencing pitch deposition as different combinations of pitch components led to significantly different depositions at the same temperatures and/or pHs.

Work throughout the past decade has shown that wood polysaccharides (i.e. galactoglucomannans), although not considered wood extractives, have a stabilisation effect on wood extractive colloids. This stabilisation effect has, in turn, been shown to reduce pitch deposition.[19, 78, 126-129].

Stack *et al*(1998)[24] while trying to understand the factors that affected pitch deposition using model solutions[130] demonstrated that interactions between pitch components had an influence on pitch deposition. They explained the interaction between the components in terms of the different viscosities of each of the components[64]. The work by Stack *et al*[24] was conducted at 20°C a temperature which is not common to modern papermaking conditions.

2.5 Statistical modelling of pitch component interactions

Another drawback of the Stack *et al*[24] work was that twelve pseudo three-dimensional graphs were to be interpreted in order to establish whether or not interactions between components existed.

The use of statistical modelling to understand and identify interactions between chemical components has been used since 1955; when Claringbold [131] reported a

simple statistical process by which he could model the effects that different combinations of three distinct drugs had on the joints of mice.

Though Claringbold's "simplex design" was not factorial, it did lay the groundwork for Scheffé to write "Experiments with Mixtures"[131] in 1958, which allowed for factorial models to be developed as long as they met two restrictions. Firstly, that the models were of three or more q-components. Secondly, that the x-amount (moles, litres, etc.) of each i-th component of the mixture obeyed the following restriction:

$$x_i \geq 0 (i = 1,2,\ldots,q), x_1 + x_2 + \ldots + x_q = 1.$$

Equation 2.2.

If these restrictions, Equation 2.2, were obeyed one could develop polynomial functions, or responses (η), of the n-th degree for any q-component system. These responses (η) would have:

$$\binom{n+q-1}{n} \text{ or } \frac{(n+q-1)!}{n!(q-1)!}$$

Equation 2.3.

interaction coefficients (β) and would be defined by the following models:

Linear (when n=1)

$$\eta = \sum_{1 \leq i \leq q} \beta_i x_i$$

Equation 2.4.

Quadratic (when n=2)

$$\eta = \sum_{1 \leq i \leq q} \beta_i x_i + \sum_{1 \leq i < j \leq q} \beta_{ij} x_i x_j$$

Equation 2.5.

Cubic (when n=3)

$$\eta = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \sum_{1\le i<j\le q} \gamma_{ij} x_i x_j (x_i - x_j) + \sum_{1\le i<j<k\le q} \beta_{ijk} x_i x_j x_k$$

Equation 2.6.

Modelling a response (η) for a third order (n=3), three component (q=3) mixture would yield the following polynomial (η):

$$\eta = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \gamma_{12} x_1 x_2 (x_1 - x_2)$$
$$+ \gamma_{13} x_1 x_3 (x_1 - x_3) + \gamma_{23} x_2 x_3 (x_2 - x_3) + \beta_{123} x_1 x_2 x_3$$

Equation 2.7.

The null hypothesis that Scheffé used to determine the interaction coefficients (β) was:

$$H_0 : \beta_i = 0$$

Equation 2.8.

This null hypothesis theory (Equation 2.8) was shown to describe a situation where the response (η) was dependent on the mixture components by Marquardt and Snee [132, 133], which prompted them to develop a new null hypothesis that was no longer dependent on the mixture components:

$$H_0 : \beta_i = \beta_0 \qquad \text{(linear terms)}$$
$$\beta_i = 0 \qquad \text{(other terms)}$$

Equation 2.9.

This new null hypothesis theory (Equation 2.9) states that the response (η) is a constant at all points of the "simplex centroid design"[133]. If the extremes are located at a distance that makes the squared terms in the model orthogonal (at right angles) to each other (satisfying Scheffé's second restriction), the design is called an "orthogonal composite design" or sometimes "central composite design"[134]. If any other extreme points are used then the interpretation of the model can be conducted using standard nonorthogonal regression analysis[134]. In 1971 Snee[132] stated that as

long as the constant term (β_0) was retained in the nonorthogonal regression analysis then the null hypothesis, shown in Equation 2.9, would be satisfied.

Although Stack *et al*[24] were the first to use statistical modelling to determine the interactions between pitch components other pulp and paper researchers have used these methods of statistical analysis and plotting of four dimensions[135-139].

3. METHODS

The following chapter details the laboratory techniques used during the course of this work.

3.1. Colloidal Preparation - Dialysis

In order to study the deposition of pitch from its colloidal form to its agglomerated form additional laboratory steps were needed to be taken to ensure that the initial, or pre-deposition, samples were in the colloidal form. Model pitch dispersions were prepared using a variation on methods developed by both Sundberg *et al*[130] and Stack *et al*[24].

The model pitch dispersions were made from a model solution that was a mixture of a fatty acid (oleic acid, Aldrich 99+% purity [112-80-1]), a triglyceride (triolein, Sigma 99 % purity [122-32-7]) and a resin acid (abietic acid, Aldrich 70 % purity technical grade [514-10-3]) in 8 mL of acetone (APS Ajax Finechem 99.5% purity [67-64-1]).

The model solution was added to a stirred 250mL volume of distilled water, which had been brought to pH 5 using 0.16M nitric acid (HNO_3 – BDH [7697-37-2]) and contained a low electrolyte concentration of 0.001M potassium nitrate (KNO_3 – BDH 99.5% purity [7757-79-1]). The acetone was removed by dialysis using a cellulose membrane tubing (Sigma D-9402, 76mm wide, >12,000 MW) and a wash solution of distilled water, which had been brought to pH 5 using 0.16M HNO_3 and contained a slight electrolytic residual of 0.001M KNO_3.

The model solutions were dialyzed for 24 hours, during which the wash solution was changed every 30 minutes for the first 5 hours in order to remove the acetone from the mixture. The model solutions were diluted to 400mL using fresh wash solution. The 400mL samples were adjusted to the desired pH using 0.18M potassium hydroxide (KOH Aldrich 99.99% purity [1310-58-3]) and/or 0.16M HNO_3 in order to study their depositional characteristics. Measuring of pH is further discussed in Appendix A

3.2. Deposition

Deposition was conducted, similarly to the work done by Stack *et al*[24], by stirring 400mL of the dialyzed dispersions in polyethylene (PE) jars using a paddle stirrer (Cole Palmer, PE coated) as the shear force generator. All depositions were conducted over a period of two hours at a constant temperature and shear rate, in a temperature bath with paddles stirring at a constant rate of 330 rpm. The apparatus is shown in Figure 3.1.

Figure 3.1. Deposition apparatus (temperature bath with jars and stir paddles)

3.3. Extraction

The model pitch components were extracted from the model pitch dispersions, before and after deposition, using tertiary butyl methyl ether (*t*-BME, Aldrich 99.8% purity HPLC [1634-04-4]). The pitch containing *t*-BME supernatant was pipetted off, with a Pasteur pipette, from the top of 5mL centrifuged pitch dispersion aliquots to which 100μL of internal standard had been added. The internal standard was a solution of toluene (Aldrich 99.8% HPLC [108-88-3]) which in 100μL contained ~55µg of each of the following standards: pentadecanoic acid (Aldrich 99+% [1002-84-2]), heptadecanoic acid (Sigma 99% purity [506-12-7]), 1,3-dipalmitoyl-2-oleoyl-glycerol (DOG)(Sigma 99% purity [2190-25-2]) and cholesteryl stearate (Sigma 99% purity [35602-69-8]). The pH was adjusted to 3.5 using 0.79M HNO_3 in order for

efficient triglyceride extraction[46]. This was repeated in duplicate for each of the samples both before and after the deposition studies. Checks were made in order to establish variance in results due to extraction methods.

3.4. Derivatisation - Silylation

The extracted samples were blown to dryness with laboratory air, then silylated using a combination of 100μL of pyridine (Aldrich 99+% purity [110-86-1]) and 100μL of BSA (N,O-bis(trimethylsilyl)-acetamide, Sigma 90% purity [10416-59-8]) followed by 20 minutes in a 60°C oven. The GC vials were cooled to room temperature and then filled to 1mL with toluene.

3.5. GC Analysis

The silylated samples were analysed using programmed injection temperature on-column high temperature gas chromatography with a flame ionisation detector (PVT-HTGC-FID).

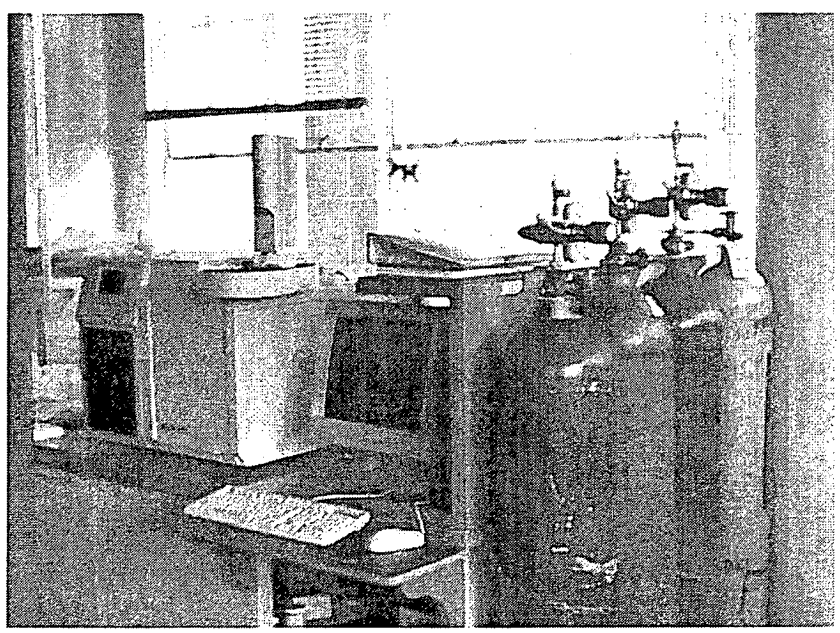


Figure 3.2. Varian 3800 GC-FID and Varian 8400 auto sampler

Samples were analysed using a Varian 3800 GC equipped with a Varian 8400 autosampler, as seen in Figure 3.2. The 1μL samples were injected onto a 15 metre Phenomenex® 100% polydimethylsiloxane (ZB-1, 15m x 0.53mm ID x 0.15μm FT) Zebron™ capillary GC column. The injector temperature was held at 90°C for the

first 30 seconds after injection and then increased to 325°C at a rate of 200°C/min. The oven/column temperature was held at 90°C for the first 1.5 minutes after injection and then increased to 320°C at a rate of 12°C/min. The FID temperature was held at 360°C for the entire duration of the ~33 minute program. This temperature program is graphically depicted in Figure 3.3. Ultra high purity helium was used as the carrier gas and the column was held at a constant pressure of 3.0psi with a corresponding linear velocity of 54.8 cm/s. The detailed software output of Varian GC analysis method is included in Appendix B.

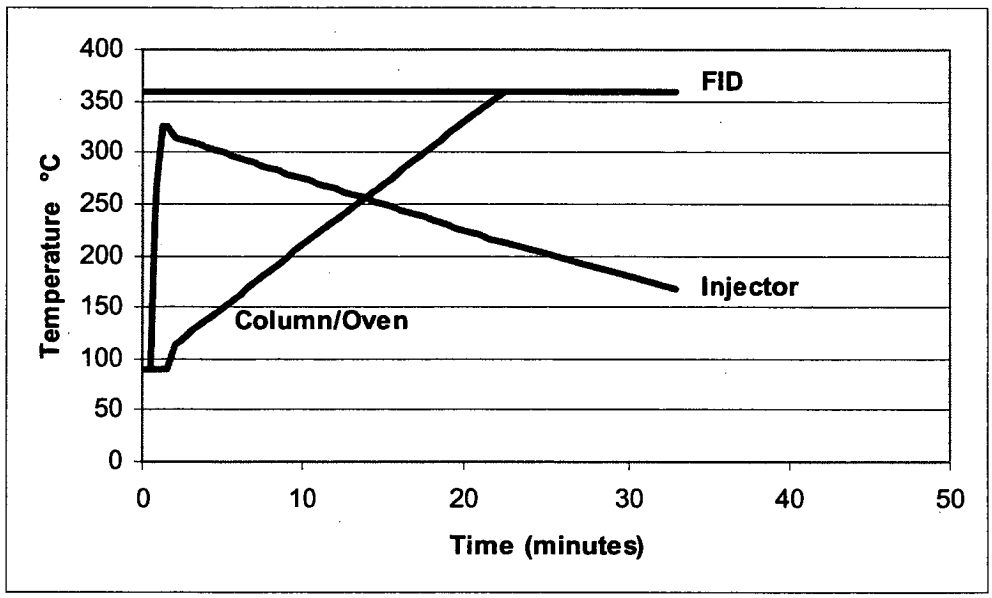


Figure 3.3. GC component temperatures during analysis.

3.6 GC Data Analysis

GC data was analysed using the Varian Star 5.5 software package. Heptadecanoic acid was selected as the internal standard, pentadecanoic acid was added to chromatographically observe whether the BSA was added, the DOG was added to help gauge the condition of the chromatographic column and the cholesteryl stearate was added as to check whether or not the internal standard had degraded during the sample extraction steps. Spikes were injected at various points throughout every sample run in order to establish FID response factors, from average peak area count ratios, for the fatty and resin acids as well as the triglycerides. The spikes were a solution of toluene which in 100μL contained ~55µg of each of the following standards: petroselinic acid (Sigma 99% purity [593-39-5]) for the fatty acids, dehydroabietic acid (Helix Biotech 99+% purity [1740-19-8]) for the resin acids and

triolein (Sigma 99% purity [122-32-7]) for the triglycerides. Checks were made in order to establish variance in results due to the GC. A GC chromatogram of the standards and spikes is shown in Figure 3.4.

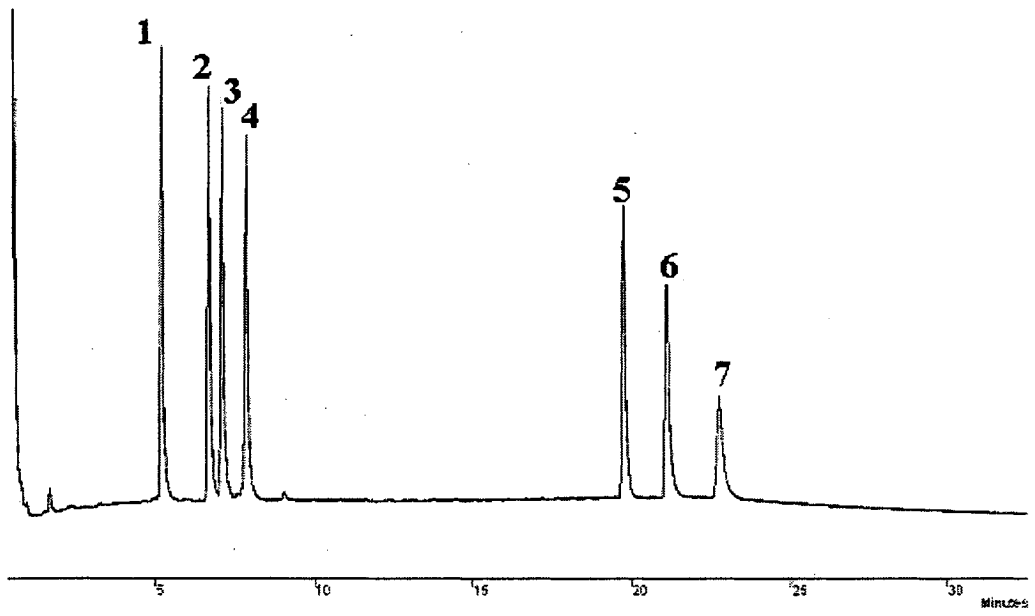


Figure 3.4. GC Chromatogram of standards and spikes. (**1** silyl ester of pentadecanoic acid, **2** silyl ester of heptadecanoic acid (IS), **3** silyl ester of petroselinic acid, **4** silyl ester of dehydroabietic acid, **5** cholesteryl stearate, **6** DOG, **7** triolein)

The averaged results from the GC injections, of the extracted samples, were used to establish the concentrations of the solutions before and after deposition. The quantity of the individual components deposited was determined by the difference between the concentrations of the solution before and after deposition. Vercoe[140] showed that this method gave results within one to two percent of those by extracting and analysing the material deposited on the walls of the deposition jar, after the deposition of an extractive mixture of which the initial and final concentrations were known.

Statistical Modelling and Model plotting

Statistical modelling was conducted using principles of general linear regression, in order to determine if, and to what extent, the components interacted with one another to form deposits. All modelling and statistical analysis was conducted through the

use of SYSTAT®10.2.05. Modelling was tested using analysis of estimates and tests of fit in order to assure their accuracy. Models were plotted using pseudo four-dimensional triangular contour plots.

3.7. Surface Tension

An Analite Surface Tension Meter was used to measure the surface tension of the samples, before and after deposition, in milliNewtons per metre (mN/m). The surface tension of the 50 mL samples was measured in a Petri dish at 20°C by lowering, and raising, the glass slide of the Meter into, and out of, the sample until the slide was just slightly submerged in the sample at which point the surface tension was recorded from the digital display[141].

4. RESULTS

This chapter presents the results of the work described by the Methods chapter. The first part deals with the analysis of pitch compounds and the second part deals with deposition behaviours.

4.1. GC Analysis Method

The initial column evaluated was a 15 metre Phenomenex® 100% polydimethylsiloxane (ZB-1, 15m x 0.53mm ID x 0.15μm FT) Zebron™ capillary GC column. The initial carrier gas chosen was ultra high purity helium at a constant flow of 5 mL/min. Maintaining constant flow at the temperatures of the analysis program resulted in inconsistent peak elution times and peak spacing. In order to maintain constant carrier gas flow the carrier gas pressure is electronically adjusted to compensate for the fact that gases expand with increases in temperature. In the first 30 seconds of a sample injection the injector temperature is increased at a rate of 200°C/sec. This high rate of temperature increase was most likely a challenge for the automated electronics attempting to adjust carrier gas pressure in order to maintain constant carrier gas flow, as a result constant carrier gas pressure was explored which allowed for carrier gas flows to vary with changes in temperature. These constant carrier gas pressure explorations are listed in Table 4.1.

Table 4.1. GC Column Pressures vs. Triolein Peak Elution Time

Constant Column Pressure (psi)	Triolein Peak Elution Time (min.)
2.5	28.2
3.0	26.6
4.0	24.5
6.0	22.4
8.0	21.3
9.0	21.0

All constant carrier gas pressures provided consistent peak elution times within 0.05% from injection to injection. At a constant pressure of 2.5psi helium the peaks of the silyl ester of pentadecanoic acid and silyl ester of heptadecanoic acid were becoming crowded (i.e. near co-elution), as a result a constant column pressure of 3.0psi helium was selected. This constant pressure of 3.0psi had an initial column

flow of 6.4mL/min. It is believed that the constant pressure of 2.5psi helium was too low for the pressure control systems of the GC.

GC temperatures were based largely on the work of Örså and Holmbom[46], as seen in Table 4.2. They made use of the programmable injector temperature in their method. Difficulties with pentadecanoic double peaks, as seen in Figure 4.1, resulted in the need to examine different oven and injector temperatures. Initial injector and oven temperatures of 90°C were shown to provide the most symmetrical and narrowest peaks.

Table 4.2. GC Analysis temperatures from a variety of published works.

	Örså and Holmbom[46]	Wallis and Wearne[50]	Corin *et al*[51]
Detector	FID	FID	Mass spectroscopy
Detector temperature (°C)	340	340	300
Injector temperature (°C)	80 for 0.5 min 340 at 200/min	320	280
Oven temperature (°C)	100 for 1.5 min 340 at 12/min	100 for 3 min 340 at 5/min	100 for 2 min 300 at 8/min

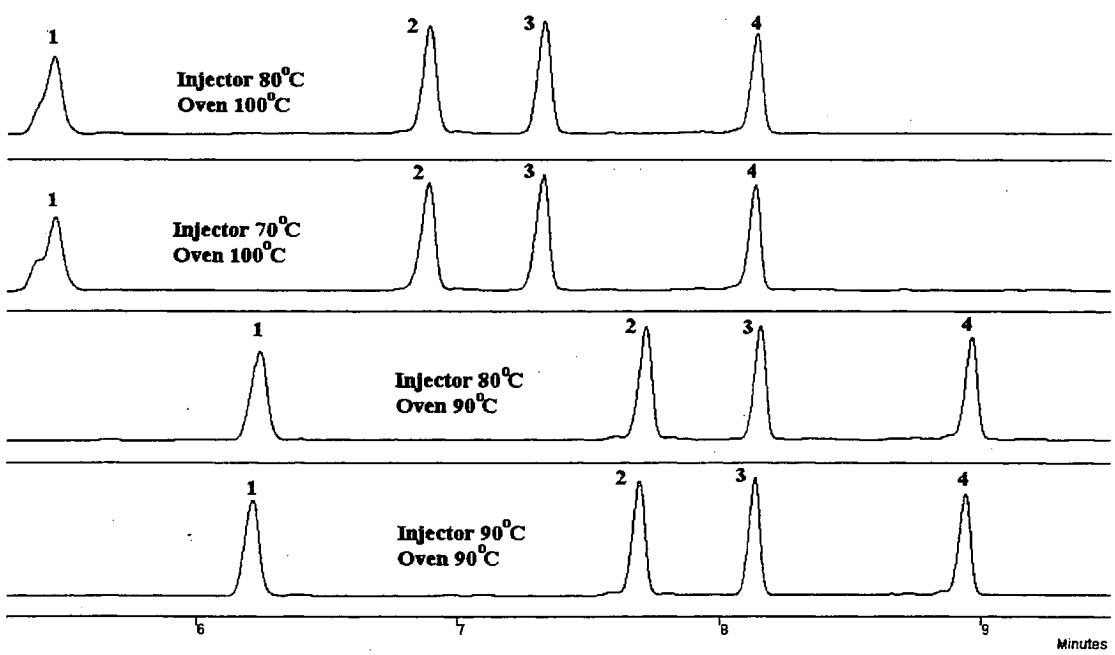


Figure 4.1. GC Chromatographs of standards and spikes at different oven and injector temperatures. (**1** pentadecanoic acid, **2** heptadecanoic acid (IS), **3** petroselinic acid, **4** dehydroabietic acid)

Sample injection volumes were explored, as shown in Table 4.3, based on published

injection volumes shown in Table 4.4.

Table 4.3. GC sample injection volumes vs. internal standard area counts

Injection Volume (µL)	Internal Standard (Area Counts)
1.00	42773
1.25	57947
1.50	66661

Table 4.4. GC injection volumes and techniques from a variety of published works.

	Örså and Holmbom[46]	Wallis and Wearne[50]
Injection volume(μL)	0.8	2
Solvent plug	0.7μL toluene	

An injection volume of 1μL provided adequate internal standard area counts and as such it was selected as the sample injection volume. The standard on-column method that came with the Varian Star 5.5 software package did not include a solvent plug. The recovery rates of the internal standard were adequate so the need for a solvent plug was not explored.

Checks were made in order to establish variance in results due to GC analysis methods. These checks of precision of the GC analysis were determined by injecting the same sample five times. These checks were conducted five separate times over the course of the deposition experiments. As each of these separate checks was conducted on samples of different component concentrations, they were normalised by dividing the standard deviation of a component concentration by its respective average concentration. This normalisation allows for the presentation of variation due to GC analysis to be expressed in terms of percent variation of each component. The relatively low range of these variations is shown in Table 4.5.

Table 4.5. Component concentration variations due to GC analysis method.

Component	Relative standard deviation (%)
Fatty Acid	+/- 0.72
Resin Acid	+/- 0.27
Triglyceride	+/- 3.40

In examining Table 4.5 one notes that triglyceride concentrations vary almost five

times more than fatty acid concentration and almost 13 times more than resin acid concentrations. All the variations however are below five percent, and very similar to overall method deviations reported by Örså and Holmbom[46].

t-BME was selected as the solvent for liquid-liquid extraction as it had been proved effective by others as seen in Table 2.3. The samples were extracted with one 2mL aliquot of *t*-BME at pH 3.5 as Örså and Holmbom[46] showed that it was optimal for triglyceride extraction. Since no thin emulsion layers existed after the first extraction, there was no need for further extractions.

Checks were made, by extracting one sample five separate times, in order to establish variance in results due to extraction methods. As with measuring variation due to GC methods, the extraction variation was measured on five separate occasions throughout deposition experimentations. The results of these variations were also normalised by dividing the standard deviation of a component concentration by its respective average concentration. The range of these variations is shown in Table 4.6. Triglyceride concentration variation due to extraction techniques was greater than five percent and approximately double the deviation of the fatty and resin acids. The deviations reported in Table 4.6 are slightly higher than the overall method deviations reported by Örså and Holmbom[46].

Table 4.6. Component concentration variations due to extraction method.

Component	Relative standard deviation (%)
Fatty Acid	+/- 2.46
Resin Acid	+/- 3.66
Triglyceride	+/- 6.65

4.2. Derivatization – Silylation Method

A variety of silylation methods had been previously published, as seen in Table 4.7, which made it difficult to choose a suitable method. As a result a variety of silylation techniques were explored. These combinations are listed in Table 4.8.

Table 4.7. Silylation techniques from a variety of published works.

	Örså and Holmbom[46]	Thurbide and Hughes[49]	Wallis and Wearne[50]	Corin et al[51]
Internal standard			Heptadecanoic acid	Heptadecanoic acid
Silylated agent	80μL BSTFA	125μL BSA	BSTFA with	100μL BSTFA
Silylating aid	40μL TCMS	200μL pyridine	1% TCMS	50μL pyridine
Silylation time (minutes)	20	20	30	
Silylation temperature(°C)	70	60	70	
Response factors				yes

Table 4.8. Silylation methods examined.

Silylation Method	A	B	C	D	E	F
Silylated agent	100μL BSTFA with	100μL BSTFA	100μL BSTFA	100μL BSA	100μL BSA	200μL BSA
Silylating aid	1% TCMS	100μL pyridine	200μL pyridine	100μL pyridine	200μL pyridine	200μL pyridine
Silylation time (minutes)	20, 30, 40, 50 and 60	20, 30, 40, 50 and 60	20, 30, 40, 50 and 60	20 and 60	20, 40 and 60	20
Silylation temperature(°C)	60	60	60	60	60	60

Each of the techniques listed in Table 4.8 were evaluated on samples containing 55.6μg of pentadecanoic acid, 54.6μg of heptadecanoic acid, 58.0μg of petroselinic acid, 55.6μg of dehydroabietic acid and 76.6μg of cholesteryl stearate. Cholesteryl stearate was selected as the internal standard as it cannot be silylated. All four analytes, though originally in 100μL of toluene, were blown dry under a stream of nitrogen before being silylated. The totals of the recovery rates of the four analytes were used as a measure to choose the final silylation method. The results of this study, which were ranked according to the total of the percent recoveries of each of the four analytes, can be seen in Table 4.9.

Table 4.9. Recovery rates of silylation methods examined.

Method from Table 4.10	Time in Oven	Pentadecanoic Acid	Heptadecanoic Acid	Petroselinic Acid	Dehydroabietic Acid	Total
F	20	86%	85%	100%	107%	377%
D	20	86%	84%	99%	95%	365%
E	60	86%	86%	98%	94%	364%
A	30	91%	92%	93%	83%	360%
C	50	88%	88%	93%	82%	352%
C	30	89%	88%	92%	81%	350%
D	60	86%	86%	89%	87%	348%
C	60	88%	87%	92%	81%	348%
A	60	87%	87%	91%	82%	346%
E	20	86%	85%	95%	80%	346%
B	60	86%	86%	91%	81%	344%
A	40	86%	88%	90%	81%	344%
C	40	87%	86%	90%	80%	343%
E	40	85%	84%	95%	79%	343%
B	30	85%	85%	91%	81%	343%
B	20	87%	87%	89%	79%	343%
C	20	87%	87%	89%	79%	342%
B	50	86%	86%	89%	79%	341%
B	40	86%	85%	89%	79%	339%
A	20	85%	85%	87%	78%	334%
A	50	84%	84%	87%	78%	333%

Although this comparison of methods could be conducted through more rigorous statistical techniques it does highlight that using equal volumes of pyridine and BSA at 60°C for 20 minutes is an acceptable technique and as such no further silylation method comparisons were conducted. The silylation method used to analyse all deposition solutions throughout the remaining experiments of the thesis were as follows; 100µL BSA and 100µL pyridine, for 20 minutes in 60°C oven (i.e. Method D).

4.3. Depositions

Experimental Design

The pre-deposition extractive concentrations targeted for experimentation were selected in an attempt to target concentration found in the waters of the paper machine head box at the Norske-Skog Albury mill. Figure 4.2 is of extractive data from the Albury mill head box water from 2001-2002 during which the target pH

was changed from 5.5 to 7.0. The raw experimental data that did not observe maximum and minimum concentration variations shown in Figure 4.2 was truncated. These truncations were made to ensure that the data set being modelled was representative of depositions occurring at the Albury plant.

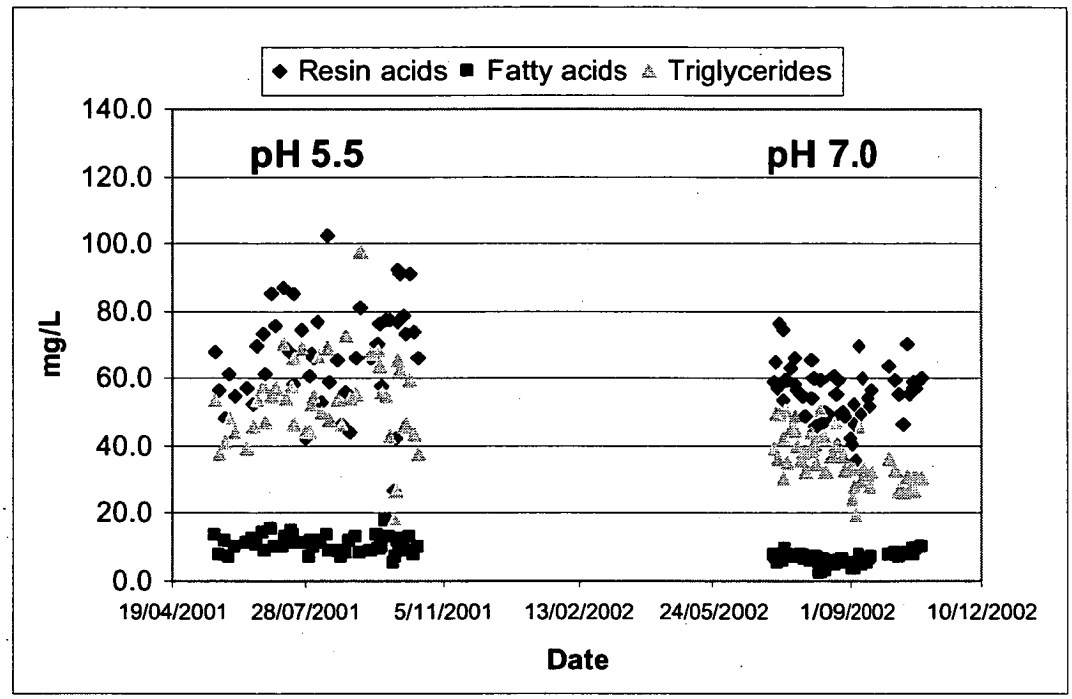


Figure 4.2. Pitch component data from the paper machine head box at Norske-Skog Albury mill.

The target modelling truncated concentrations of Table 4.10 were based on the extractive levels found in Figure 4.2. A larger concentration range, and higher concentrations, of extractives were examined in the deposition experiments in order to develop robust models capable of predicting what would happen if the triglycerides were hydrolysed to fatty acids. These limits establish the extreme vertices of each of the components.

Table 4.10. Component concentrations considered for modelling.

Component	Maximum modelling concentration (mg/L) at pH 5.5	Albury concentrations (mg/L) at pH 5.5 (Fig. 4.2)	Maximum modelling concentration (mg/L) at pH 7.0	Albury concentrations (mg/L) at pH 7.0 (Fig. 4.2)
Resin acid	90	67.3 +/- 15.0	60	56.3 +/- 8.2
Fatty acid	60	10.9 +/- 2.5	60	6.6 +/- 1.6
Triglyceride	90	53.7 +/- 13.1	60	36.2 +/- 7.6

Following the nonorthogonal general linear regression[134] models based on mixture design experiments[142] and given the concentration limits (i.e. extreme vertices [143]) of the three deposition components as set in Table 4.10 one would need as a minimum the fifteen deposition experiments outlined in Figure 4.3 and Figure 4.4 for pH 5.5 and pH 7.0 respectively.

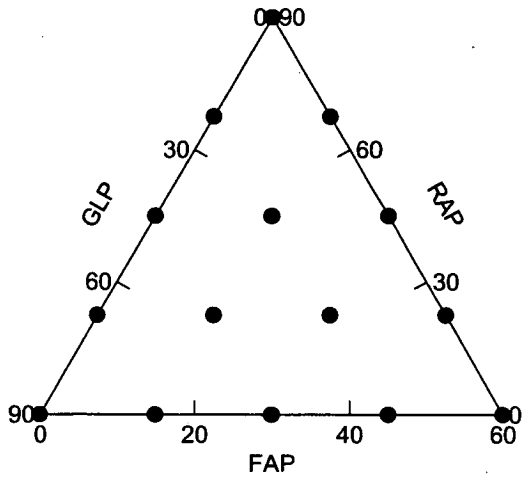


Figure 4.3. Data points needed for pH 5.5

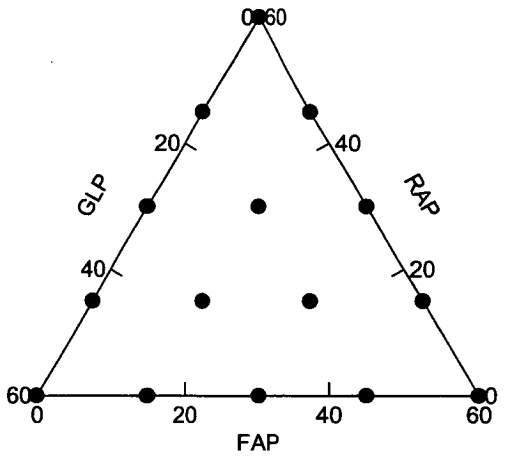


Figure 4.4. Data points needed for pH 7.0

Deposition behaviour at pH5.5, 50 ℃

A total of 139 depositions containing unique concentrations of the fatty acid, resin and triglyceride were conducted at pH 5.5, 50°C of which 23 were removed as they did not meet the modelling parameters as described in Table 4.10. Of the 116 depositions remaining, five were selected from separate deposition studies and were set aside to test the final model, leaving 111 sets of data to be used for modelling. A graphical representation of all the deposition studies, minus the five test cases, and the truncated set of deposition studies can be found in Figure 4.5 and Figure 4.6, respectively.

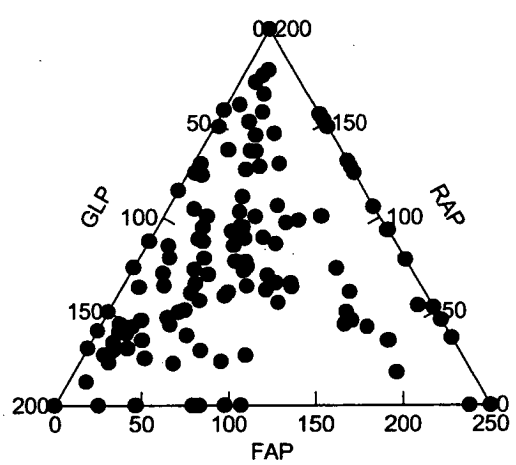


Figure 4.5. Raw data (pH5.5, 50°C)

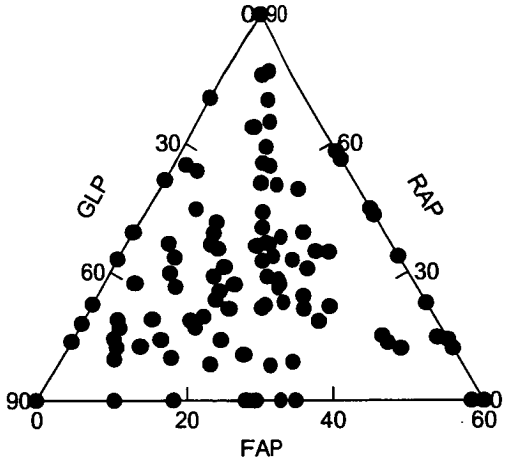


Figure 4.6. Truncated data (pH5.5, 50°C)

Statistical Modelling – Model Selection

Equation 4.1 was used as the starting point for 5 separate statistical models.

$$TPD = \beta_0 + \beta_1 FAP + \beta_2 RAP + \beta_3 GLP + \beta_4 FAP \cdot RAP + \beta_5 FAP \cdot GLP + \beta_6 RAP \cdot GLP$$

$$+ \beta_7 FAP^2 + \beta_8 RAP^2 + \beta_9 GLP^2$$

Equation 4.1.

Where:

TPD = Total pitch deposited in mg/L
FAP = Fatty acid (oleic acid) concentration before deposition in mg/L.
RAP = Resin acid (abietic acid) concentration before deposition in mg/L.
GLP = Triglyceride (triolein) concentration before deposition in mg/L.

The regression coefficients (β_i), F-ratios, residuals (e_i), R^2 and R_A^2 of each model were determined using the general linear model estimating option within SYSTAT®10.2.05. These parameters were used to evaluate and select the final statistical model, where F-Ratio is the ratio between treatment mean square and error mean square, R^2 is the coefficient of determination and R_A^2 is the adjusted coefficient of determination that compares the variance estimates both with and without explanatory variables[144].

The first model was one, which included the calculation of all of the regression coefficients (β_0 through β_9). The "tolerance" option within SYSTAT®10.2.05 was set at 1.0e-11 to give warning if any of the regressors were directly or highly correlated to the independent variable (*TPD*). The second model was one, which excluded the constant term (β_0). In order for the test of fit statistics to be properly calculated the "mixture model" option of SYSTAT®10.2.05 was used.[133] The third model was one in which regression terms of low significance ($\alpha \leq 0.05$) were removed from the model and the remaining regression coefficients were recalculated. This was repeated until all of the remaining regression terms had a high degree of significance ($\alpha \geq 0.05$). The fourth model was developed in two separate steps. The first step was one in which regression terms of low significance ($\alpha \leq 0.05$) and the constant term (β_0) were removed from the model and the remaining regression coefficients were recalculated. This was repeated until all of the remaining regression terms had a high degree of significance ($\alpha \geq 0.05$). The second step was one in which the remaining regressors from the first step were used to calculate for the proper test of fit statistics as part of the "mixture model" option. The fifth model was one in which the regressors from the fourth model and the constant term (β_0) were used to calculate the new set of regression coefficients. These five models are listed in Table 4.11.

Table 4.11. Statistical methods used to model deposition data.

Model 1	β_0 through β_9
Model 2	β_1 through β_9
Model 3	$\alpha \geq 0.05$ for β_0 through β_9
Model 4	$\alpha \geq 0.05$ for β_1 through β_9
Model 5	Model 4 with β_0

The five potential deposition models for pH 5.5, 50°C, their regression coefficients (β_i), F-ratios, R^2 and R_A^2 values are listed in Table 4.12.

Table 4.12. Summary of pH5.5, 50°C model regressors and fit statistics

	Model 1	Model 2	Model 3	Model 4	Model 5
β_0	5.617		6.024		3.607
β_1	0.224	0.421	0.239	0.363	0.258
β_2	0.477	0.652	0.477	0.708	0.595
β_3	0.053	0.151		0.110	0.074
β_4	-0.010	-0.011	-0.009	-0.010	-0.009
β_5	-0.006	-0.008	-0.006	-0.008	-0.006
β_6	0.003	0.002	0.004		
β_7	0.001	-0.001			
β_8	0.008	0.007	0.008	0.006	0.007
β_9	-0.001	-0.001			
F-ratios	65.157	71.605	100.377	115.761	97.315
R^2	0.853	0.849	0.853	0.846	0.849
R_A^2	0.840	0.837	0.844	0.839	0.840

Of the five models shown in Table 4.12 all have very favourable F-ratios, R^2 and R_A^2 values, which made selecting a final model rather difficult. The final model selected was Model 4 because it had the highest product of F-ratio and R_A^2 values.

Model Testing

In order to ensure that the selected model was accurate it was tested in three separate ways. Firstly, the residuals (e_i) were plotted against *TPD*, the modelled *TPD* and against each of the regressors in order to ensure that patterns did not exist, thus satisfying the modelling conditions. Secondly, the modelled *TPD* data calculated using experimental *FAP*, *RAP* and *GLP* data was plotted against the actual *TPD* data using SYSTAT®10.2.05's "Outliers and Influence (Linear Regression)" in order to test the scatter of the statistical models. The R^2 of the second test was also determined. Lastly, the data from five depositions, not used for statistical modelling, was used to test the predictability of the statistical models (as determined by R^2). These three tests are listed in Table 4.13.

Table 4.13. Statistical methods used to model deposition data.

Test 1	Plot residuals vs. regressors, TPD and Model
Test 2	Plot TPD vs. Modelled TPD (R^2)
Test 3	Test model with data from five independent depositions (R^2)

Test 1 - Plot residuals (e_i) vs. regressors (β_i), TPD and Modelled TPD

The residuals (e_i) were plotted against *TPD*, the modelled *TPD* and against each of the regressors in Figure 4.7 in order to observe whether patterns in the many comparisons of the Scatter Plot Matrix (SPLOM) of SYSTAT®10.2.05 existed.

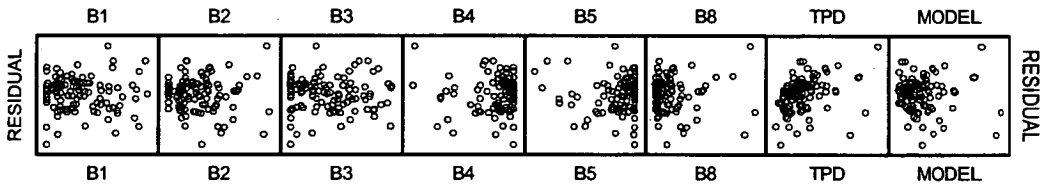


Figure 4.7. SPLOM of Model 4 pH 5.5, 50°C

In examining the many X-Y plots in the SPLOM of Figure 4.7 one observes no noticeable patterns, thus satisfying the modelling conditions of Model 4.

Test 2 - Plot TPD vs. Modelled TPD

The level of correlation between the *TPD* and the modelled *TPD*, with a R^2 of 0.8469, is quite evident in looking at Figure 4.8.

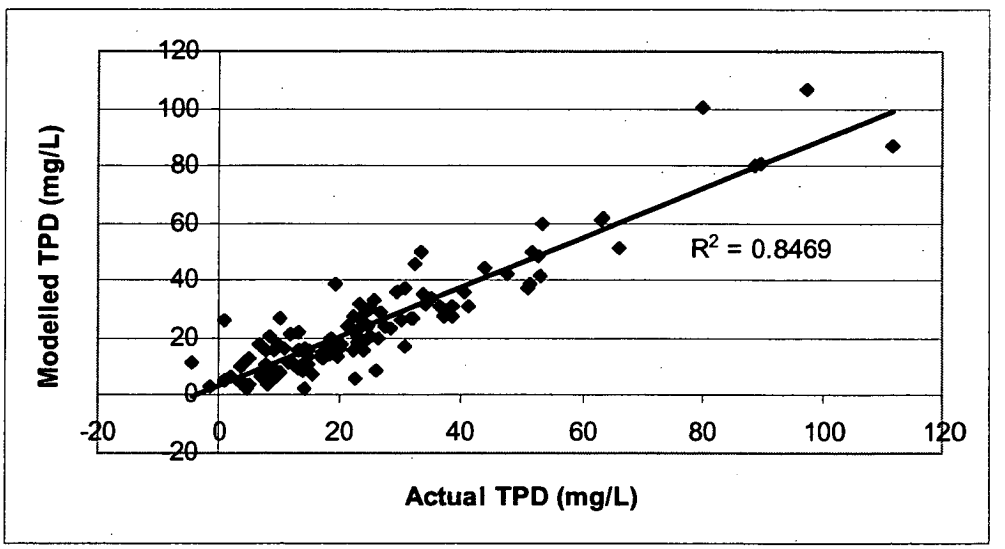


Figure 4.8. X-Y plot of modelled *TPD* vs. the *TPD* of the experiments.

Further examination of the correlation between modelled *TPD* and *TPD* is done by examining the Cook's distances (D_i)[145] and outliers[146] in their X-Y plot, as seen in Figure 4.9, which take into account studentised residuals and the variance of

residuals. The larger the diameter of the data points the larger the influence of that data point on the statistical model. If a data point is an influential case or an outlier SYSTAT®10.2.05 shades in the plotted data point. There are a few data points of concern from an influential standpoint and they are all located at the higher levels of *TPD*. The remaining data points are quite small and do follow the slope of the relationship.

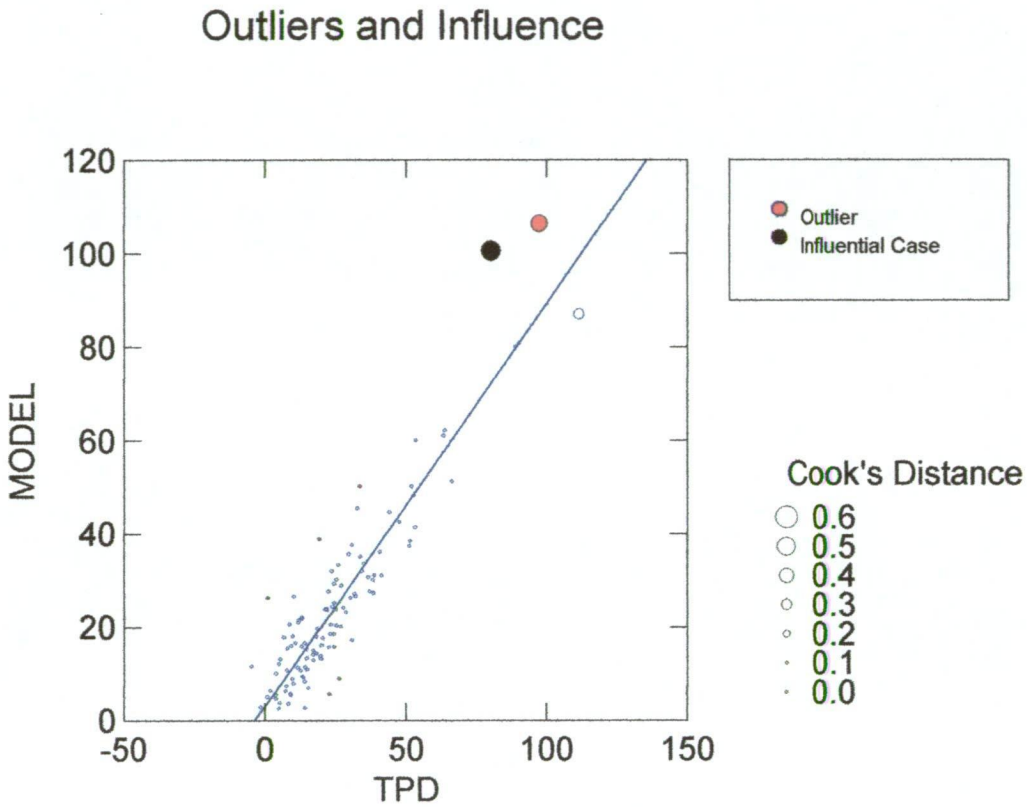


Figure 4.9. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Test 3 - Test model against data from five independent depositions

Five independent data points, shown in Figure 4.10, were used to test the predictability of Model 4. The actual *TPD* of the five data sets were plotted against the modelled *TPD* of the data points, the results of which are shown in Figure 4.12 indicating a high level of predictability with an R^2 value of 0.9218.

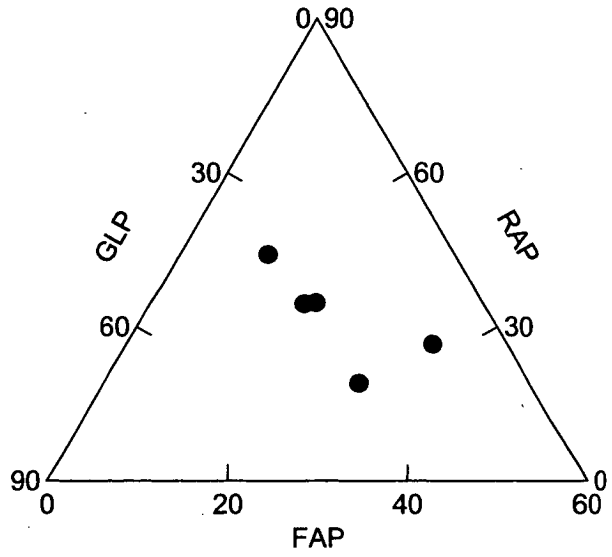


Figure 4.10. Independent deposition tests

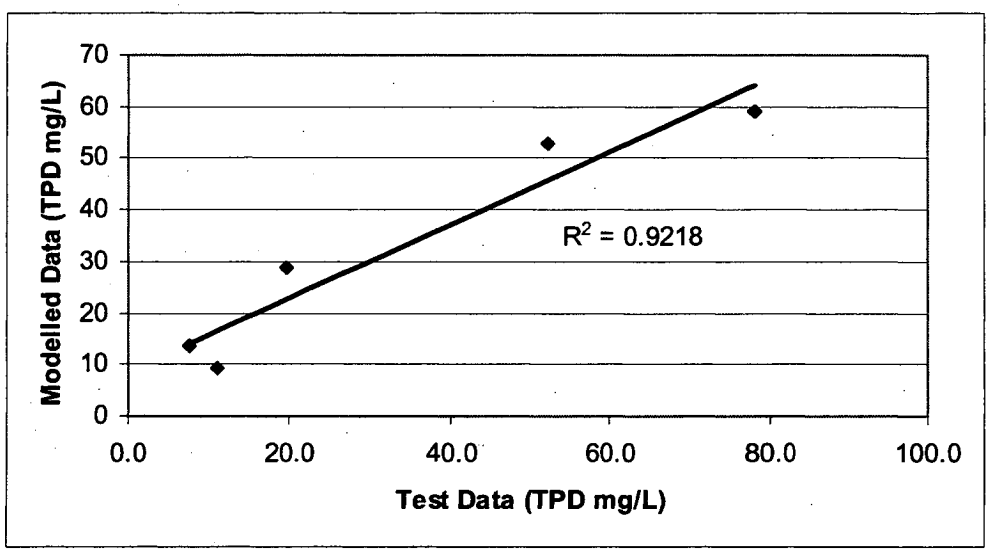


Figure 4.11. X-Y plot of modelled *TPD* of the test data vs. the *TPD* of the test data.

Triangular coordinate contour plot of the model surface

The surface of the model for the pH 5.5, 50°C deposition data is shown in Figure 4.12. It can be observed that deposition increases, as the system becomes primarily resin acid.

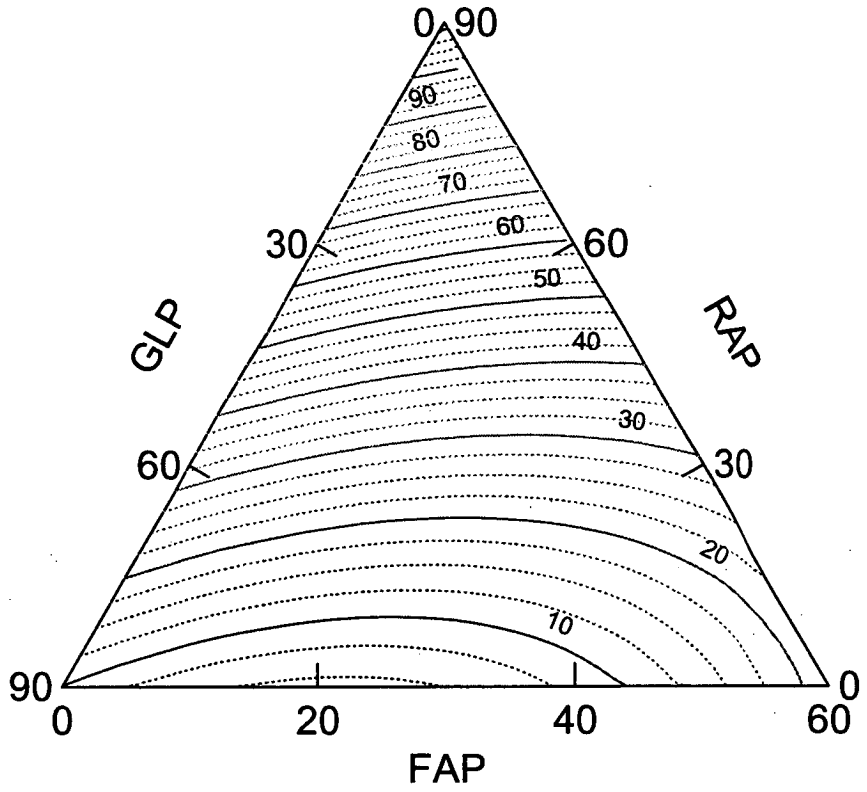


Figure 4.12. Triangular coordinate contour plot of the surface of model 4. (The contour lines indicate modelled *TPD,* all units are in mg/L.)

Raw data, test data and raw modelling results for pH 5.5, 50°C are included in Appendix C.

Deposition behaviour at pH5.5, 20 ℃

76 depositions containing unique concentrations of the fatty acid, resin and triglyceride were conducted by Stack *et al*[24], at pH 5.5, 20°C. This data was used to determine a model at pH 5.5, 20°C. Their experiments were conducted using the same methods as depositions at pH 5.5, 50°C. From the data set, 11 points were removed as they did not meet the modelling parameters as described in Table 4.10. Of the 65 depositions the remaining five were selected from separate deposition studies and were set aside to test the final model, leaving 60 sets of data to be used for modelling. A graphical representation of all the deposition studies, minus the five test cases, and the truncated set of deposition studies can be found in Figures 4.13 and 4.14 respectively.

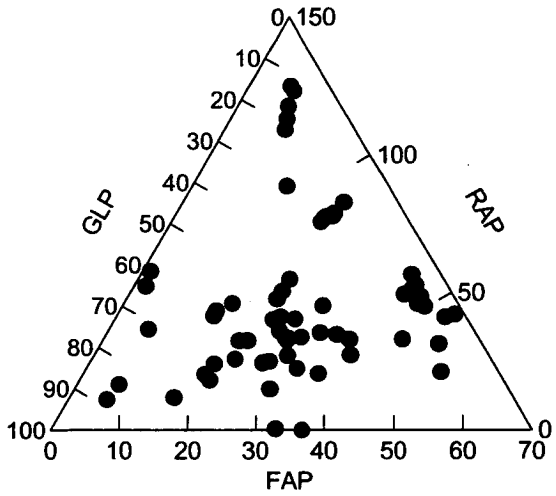


Figure 4.13. Raw data (pH5.5, 20°C)

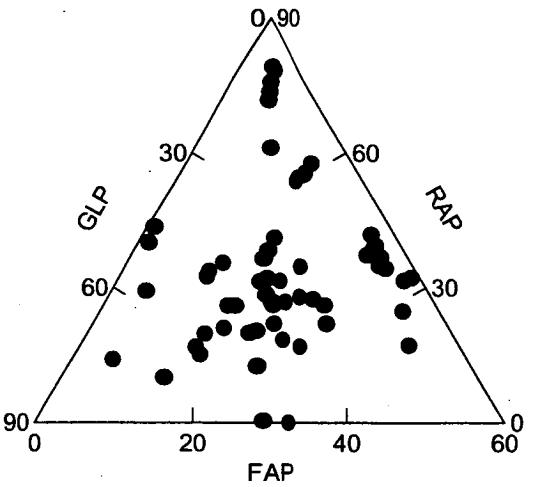


Figure 4.14. Truncated data (pH5.5, 20°C)

Please note that there are very few data points in Figure 4.16 that appear on the axes which highlight the absence of single component deposition studies conducted by Stack *et al*[24]. The consequences of this will be explained in the discussion section.

Statistical Modelling – Model Selection

Statistical modelling of the data was carried out. The results of the five models are shown in Table 4.14.

Table 4.14. Summary of pH5.5, 20°C model regressors and fit statistics

	Model 1	Model 2	Model 3	Model 4	Model 5
β_0	10.596		12.865		9.818
β_1	-0.063	0.408			
β_2	-0.013	0.230		0.319	-0.002
β_3	0.274	0.482		0.631	0.279
β_4	0.040	0.035	0.041	0.038	0.039
β_5	-0.023	-0.028	-0.023	-0.025	-0.024
β_6	0.014	0.012	0.013	0.010	0.014
β_7	-0.016	-0.019	-0.018	-0.015	-0.016
β_8	-0.003	-0.004	-0.003	-0.005	-0.003
β_9	-0.005	-0.006		-0.008	-0.005
F-ratios	37.072	40.270	67.610	44.701	42.516
R^2	0.870	0.863	0.862	0.857	0.870
R_A^2	0.846	0.842	0.850	0.838	0.849

All the models were found to have very favourable F-ratios, R^2 and R_A^2 values which

made selecting a final model rather difficult. The final model selected was Model 3 because it had the highest combination of F-ratios and R_A^2 values.

Model Testing

Test 1 - Plot residuals (e_i) vs. regressors (β_i), TPD and Modelled TPD

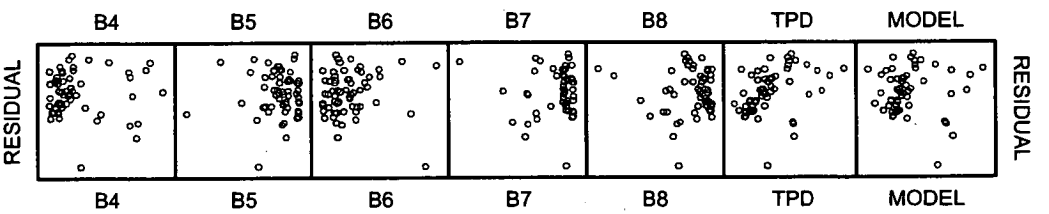


Figure 4.15. SPLOM of Model 3 pH 5.5, 20°C

Figure 4.15 shows the X-Y plots in the SPLOM of Model 3 at pH 5.5 and 20°C. No noticeable patterns are evident, thus satisfying the modelling conditions of Model 3.

Test 2 - Plot TPD vs. Modelled TPD

The level of correlation between the *TPD* and the modelled *TPD* is quite evident in looking at Figure 4.16 with a R^2 of 0.8632.

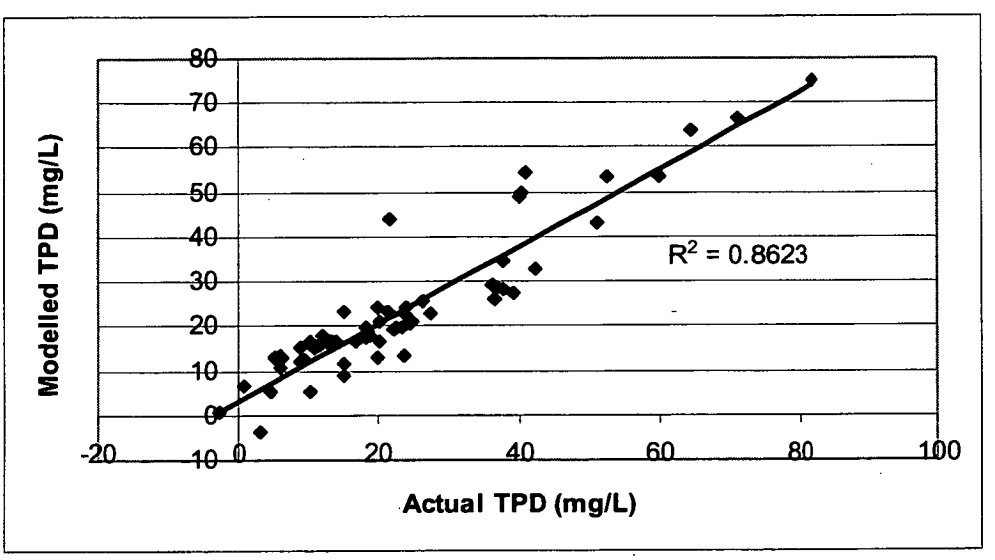


Figure 4.16. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Further examination of the correlation between modelled *TPD* and *TPD* shows that there are three data points of concern, within Figure 4.17, from an influential standpoint and they are all located at moderate levels of *TPD*. The remaining data points do however follow the slope of the relationship.

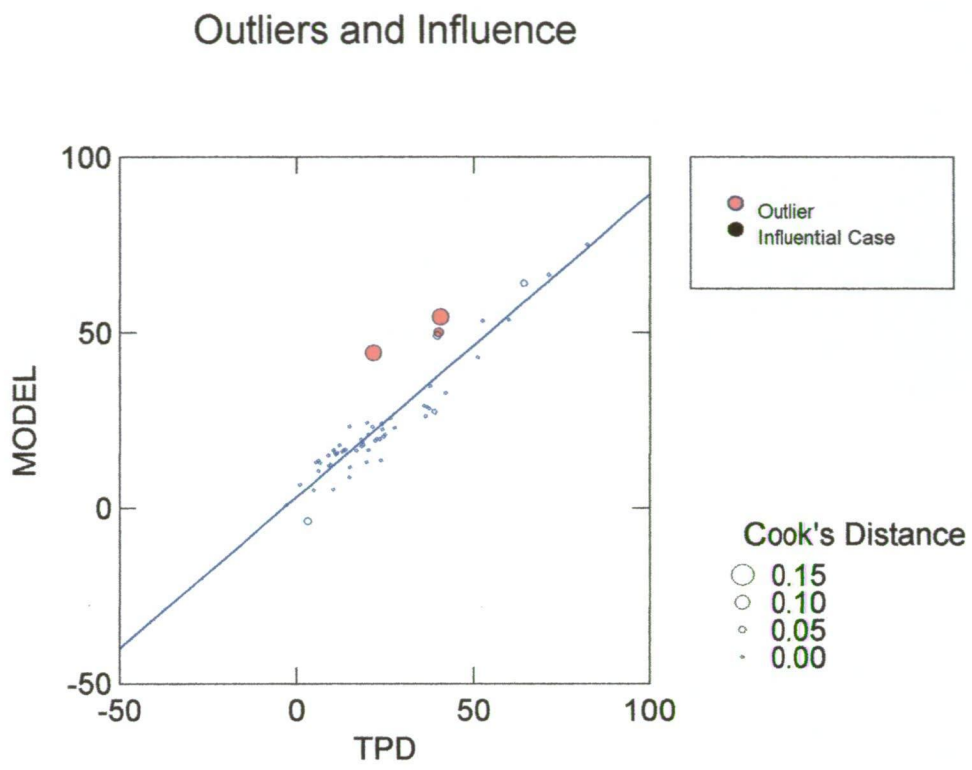


Figure 4.17. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Test 3 - Test model against data from five independent depositions

Five independent data points, shown in Figure 4.18, were used to test the predictability of Model 3. The actual *TPD* of the five data sets were plotted against the modelled *TPD* of the data points, the results of which are shown in Figure 4.19 indicating a high level of predictability with an R^2 value of 0.852.

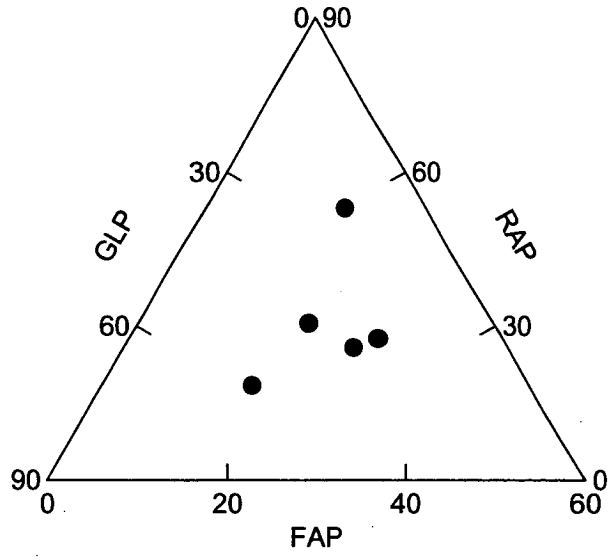


Figure 4.18. Independent deposition tests

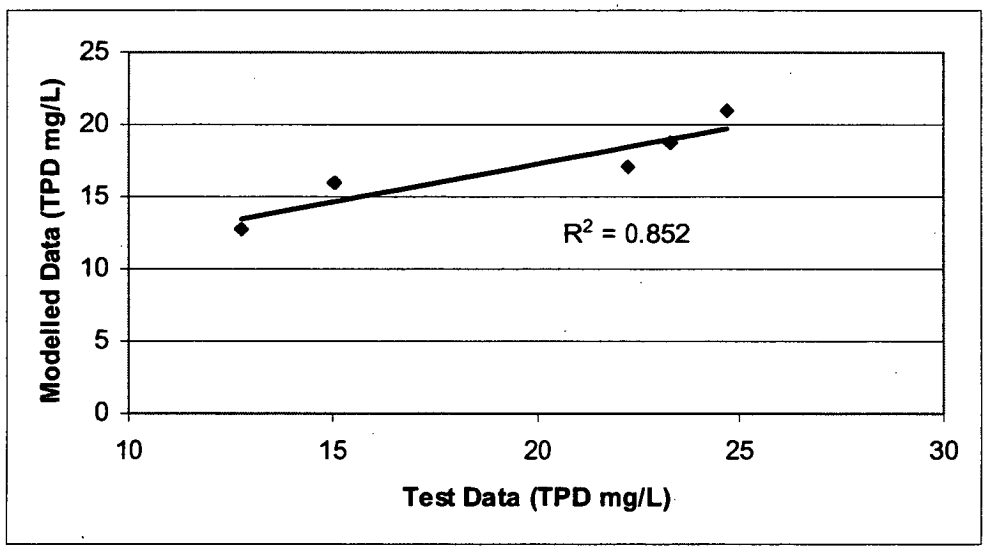


Figure 4.19. X-Y plot of modelled *TPD* of the test data vs. the *TPD* of the test data.

Triangular coordinate contour plot of the model surface

The surface of the model for the pH 5.5, 20°C deposition data is shown in Figure 4.20. Two noteworthy observations can be made. First, that the highest deposition (~40mg/L) occurs when medium resin acid levels (~50mg/L) are coupled with moderate to high levels of fatty acid (>20mg/L) and low triglyceride levels (<30mg/L). This area of deposition is shown as a hump of contour line values along the resin acid axis. Secondly, that when fatty acid, triglyceride or a combination of the two are present, there is less pitch deposition (<20mg/L). The lower half of

Figure 4.20 represents this area of lower TPD. There is another area of lower deposition and it is located at the top of the triangular plot, where the system is primarily resin acid.

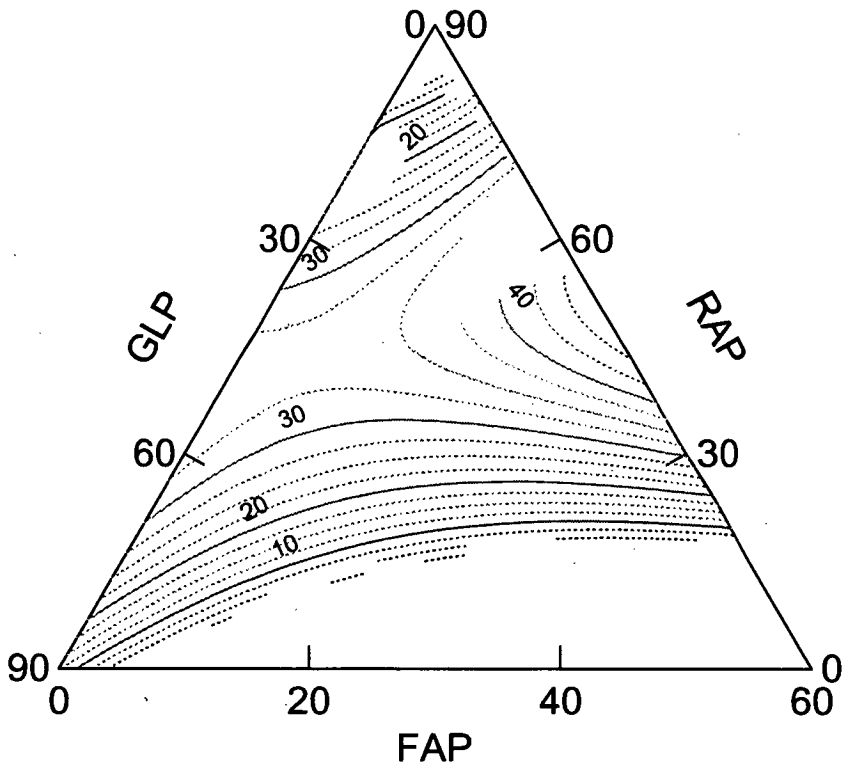


Figure 4.20. Triangular coordinate contour plot of the surface of model 3. (The contour lines indicate modelled *TPD,* all units are in mg/L.)

Raw data, test data and raw modelling results for pH 5.5, 20°C are included in Appendix D.

Deposition behaviour at pH 7.0, 50°C

A total of 65 depositions containing unique concentrations of the fatty acid, resin and triglyceride were conducted at pH 7.0, 50°C of which none were removed as all the data from the depositions satisfied the modelling parameters as described in Table 4.10. 5 depositions were set aside to test the final model, leaving 60 sets of data to be used for modelling. A graphical representation of the deposition study data can be found in Figure 4.21.

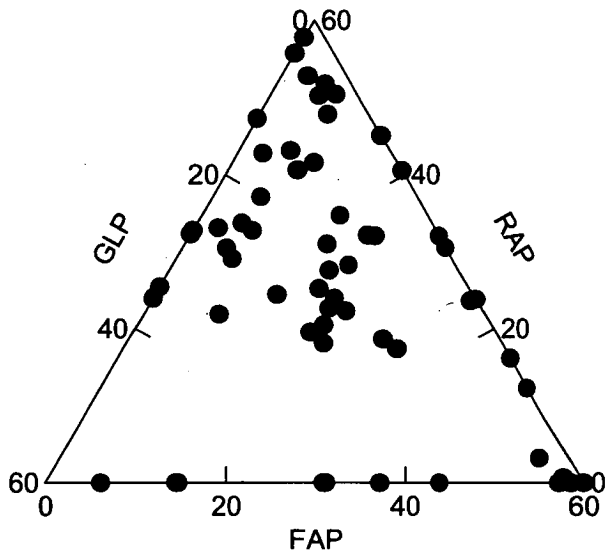


Figure 4.21. Deposition data pH 7.0, 50°C

Please note the absence of data in the lower left of Figure 4.21, representing data of high triglyceride concentrations. This will be explained further in the discussion section.

Statistical Modelling – Model Selection

Table 4.15 summarises the regression coefficients and statistics for the five models.

Table 4.15. Summary of pH7.0, 50°C model regressors and fit statistics

	Model 1	Model 2	Model 3	Model 4	Model 5
β_0	1.021		7.376		3.710
β_1	0.541	0.582		0.389	0.247
β_2	0.073	0.119			
β_3	0.063	0.097			
β_4	-0.005	-0.006			
β_5	-0.010	-0.010		-0.018	-0.014
β_6	-0.008	-0.008		-0.011	-0.009
β_7	-0.006	-0.006			
β_8	0.017	0.016	0.012	0.020	0.017
β_9	0.009	0.008	0.004	0.014	0.011
F-ratios	8.492	9.732	29.035	17.939	15.355
R^2	0.605	0.604	0.505	0.566	0.587
R_A^2	0.533	0.542	0.487	0.535	0.549

Of the five models shown in Table 4.15 Models 1, 2, 3 and 4 all have moderately

favourable F-ratios, R^2 and R_A^2 values which made selecting a final model rather difficult. The final model selected, from the remaining four models, was Model 5 because it had the highest R_A^2.

Model Testing

Test 1 - Plot residuals (e_i) vs. regressors (β_i), TPD and Modelled TPD

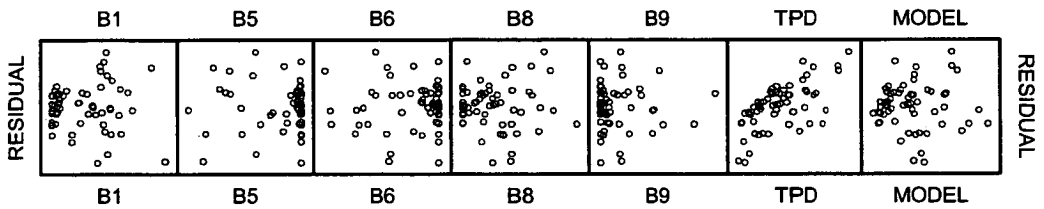


Figure 4.22. SPLOM of Model 5 pH 7, 50°C

The X-Y plots in the SPLOM of Figure 4.22 show no noticeable patterns, thus satisfying the modelling conditions of Model 5.

Test 2 - Plot TPD vs. Modelled TPD

The level of correlation between the *TPD* and the modelled *TPD* is somewhat evident in looking at Figure 4.23 with a R^2 of 0.5871.

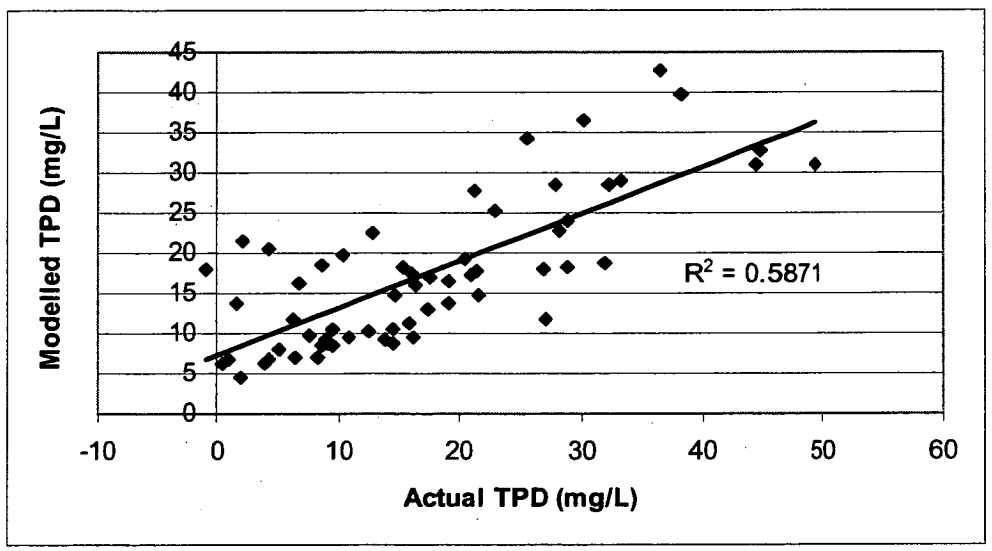


Figure 4.23. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Further examination of the correlation between modelled *TPD* and *TPD* shows that there are seven data points of concern, within Figure 4.24, from an influential standpoint and they are located throughout the range of *TPD*. The data points do however follow the slope of the relationship, though at considerable distance.

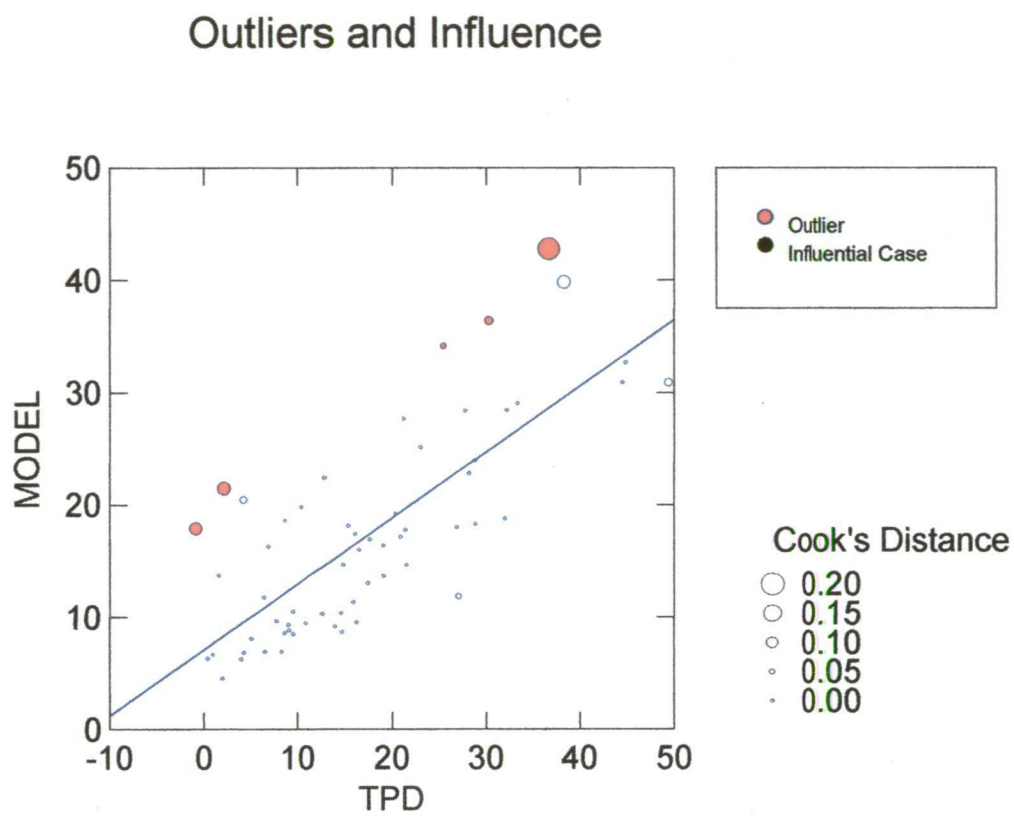


Figure 4.24. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Test 3 - Test model against data from five independent depositions

Five independent data points, shown in Figure 4.25, were used to test the predictability of Model 5. The actual *TPD* of the five data sets were plotted against the modelled *TPD* of the data points, the results of which are shown in Figure 4.26 indicating a poor level of predictability with an R^2 value of 0.221.

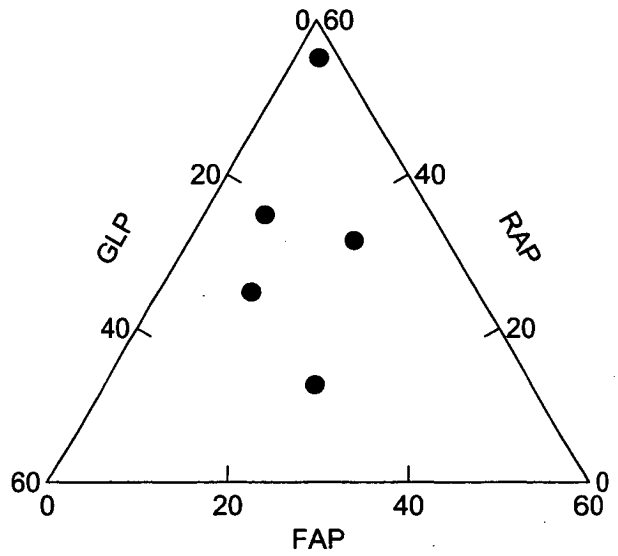


Figure 4.25. Independent deposition tests

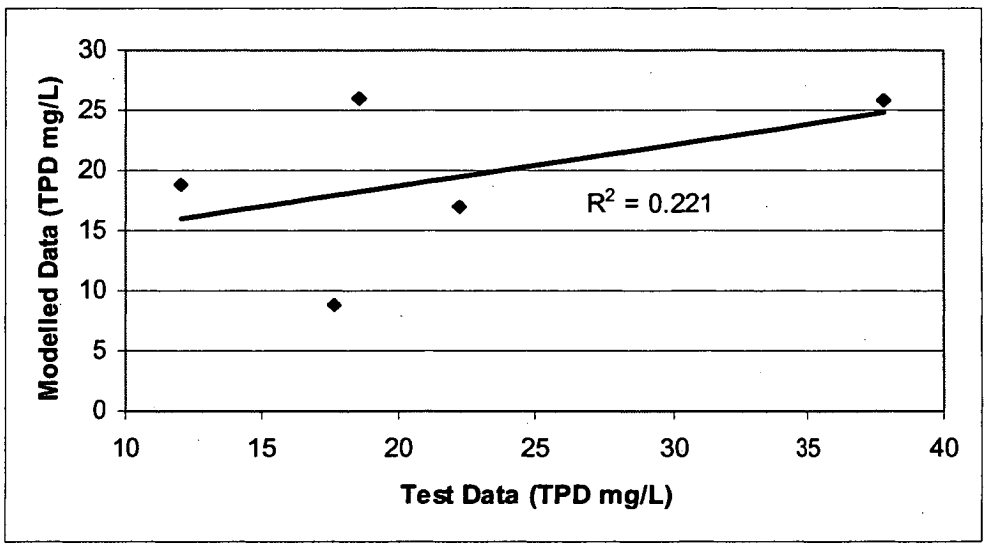


Figure 4.26. X-Y plot of modelled *TPD* of the test data vs. the *TPD* of the test data.

Triangular coordinate contour plot of the model surface

The surface of the model for the pH 7.0, 50°C deposition data is shown in Figure 4.27. From Figure 4.27 it can be observed that deposition increases when the solution moves away from a specific composition of fatty acid (~35mg/L), resin acid (~5mg/L) and triglyceride (~20mg/L). As the solution becomes primarily resin acid or primarily triglyceride deposition increases (>30mg/L).

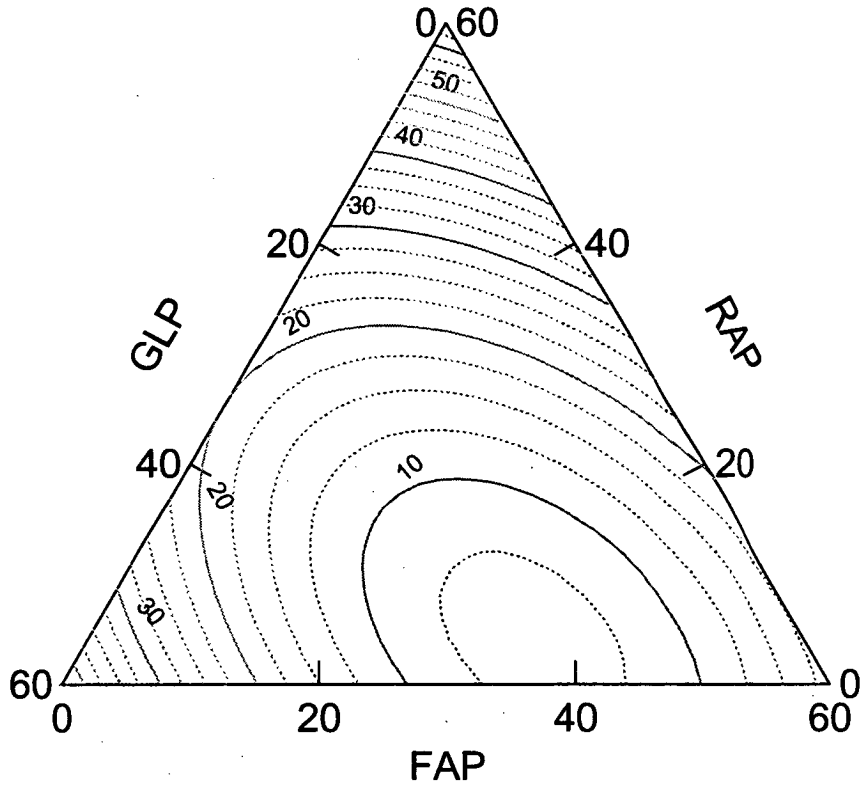


Figure 4.27. Triangular coordinate contour plot of the surface of model 5. (The contour lines indicate modelled *TPD,* all units are in mg/L.)

Raw data, test data and raw modelling results for pH 7.0, 50°C are included in Appendix E.

Deposition behaviour at pH7.0, 20°C

Stack et al [24] conducted a total of 25 depositions containing unique concentrations of the fatty acid, resin and triglyceride at pH 7.0, 20°C. Statistical modelling was carried out using this data to determine models at pH 7.0, 20°C. None of the data sets from the 25 depositions were removed as all the data from the depositions satisfied the modelling parameters as described in Table 4.10. Five depositions were set aside to test the final model, leaving 20 sets of data to be used for modelling. A graphical representation of the deposition study data can be found in Figure 4.28.

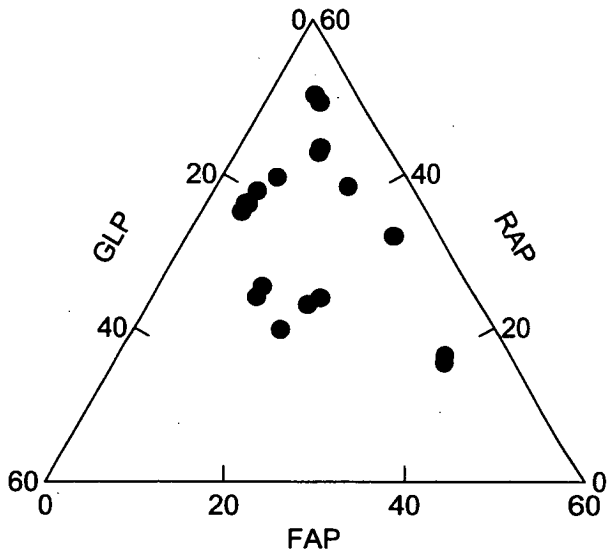


Figure 4.28. Deposition data pH 7.0, 20°C

Please note that there are very few data points in Figure 4.28 particularly in the lower half of the trigonal plot. Note that no points appear on the axes which highlights the absence of single component deposition studies conducted by Stack *et al*[24]. The consequences of this lack of data will be explained in the discussion section.

Statistical Modelling – Model Selection

The results of the five statistical models are shown in Table 4.16.

Table 4.16. Summary of pH7.0, 20°C model regressors and fit statistics

	Model 1	Model 2	Model 3	Model 4	Model 5
β_0	-4.476		-13.182		-7.461
β_1	2.768	2.573	1.221	1.192	1.223
β_2	0.702	0.543	1.324	1.123	1.255
β_3	-0.763	-0.893		-1.276	-0.714
β_4	0.010	0.011			
β_5	-0.005	0.001			
β_6	-0.042	-0.039	-0.065	-0.052	-0.059
β_7	-0.043	-0.041			
β_8	0.003	0.005			
β_9	0.079	0.078	0.088	0.107	0.100
F-ratios	30.070	36.113	59.669	59.547	48.437
R^2	0.961	0.960	0.937	0.937	0.942
R_A^2	0.929	0.934	0.921	0.921	0.922

All the models were found to have very favourable F-ratios, R^2 and R_A^2 values. The final model selected was Model 4, rather than Model 3. The product of F-ratios and R_A^2 of both models were similar and in fact Model 3 had a slightly higher product of F-ratios and R_A^2. Model 4 was selected over Model 3 as it was based on mixture interaction models and such would make for easier identification of component interactions.

Model Testing

Test 1 - Plot residuals (e_i) vs. regressors (β_i), TPD and Modelled TPD

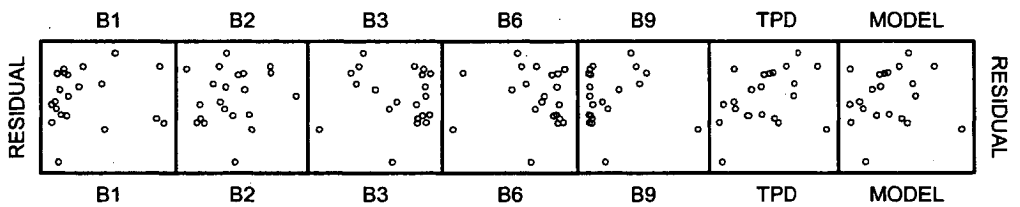


Figure 4.29. SPLOM of Model 4 pH 7, 20°C

In examining the many X-Y plots in the SPLOM of Figure 4.29 one observes no noticeable patterns, thus satisfying the modelling conditions of Model 4.

Test 2 - Plot TPD vs. Modelled TPD

The level of correlation between the *TPD* and the modelled *TPD* is quite evident in looking at Figure 4.30 with a R^2 of 0.938.

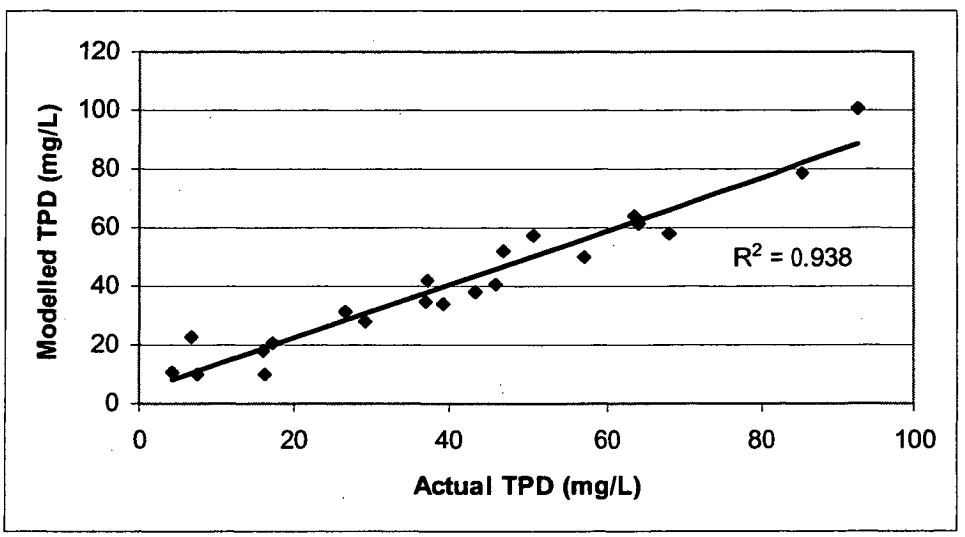


Figure 4.30. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Further examination of the correlation between modelled *TPD* and *TPD* shows that there are two data points of concern, within Figure 4.31, from an influential standpoint and they are located at high and low levels of *TPD*. The remaining data points do however follow the slope of the relationship.

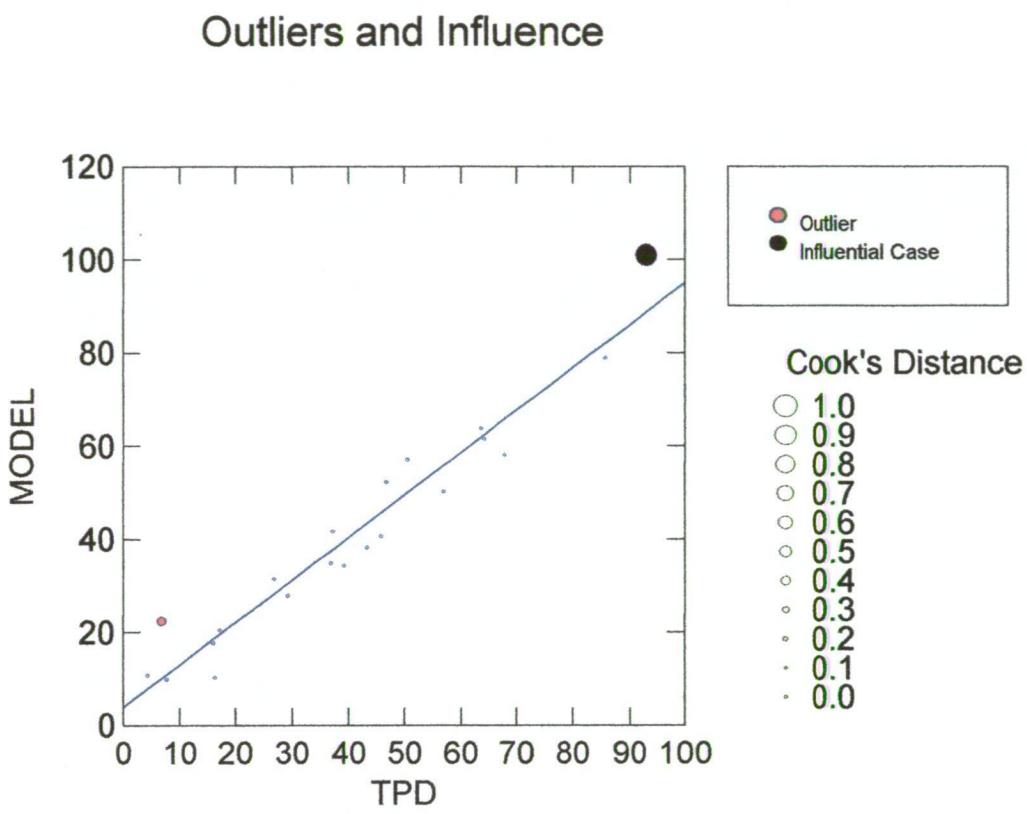


Figure 4.31. X-Y plot of the *TPD* of the model vs. the *TPD* of the experiments.

Test 3 - Test model against data from five independent depositions

Five independent data points, shown in Figure 4.32, were used to test the predictability of Model 4. The actual *TPD* of the five data sets were plotted against the modelled *TPD* of the data points, the results of which are shown in Figure 4.33 indicating a high level of predictability with an R^2 value of 0.8893.

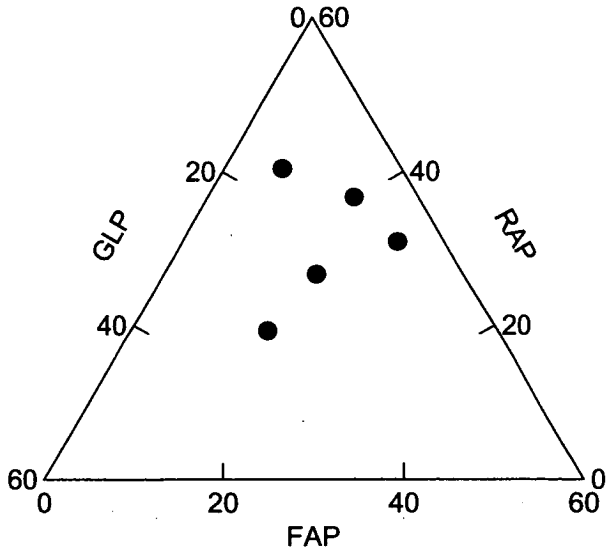


Figure 4.32. Independent deposition tests

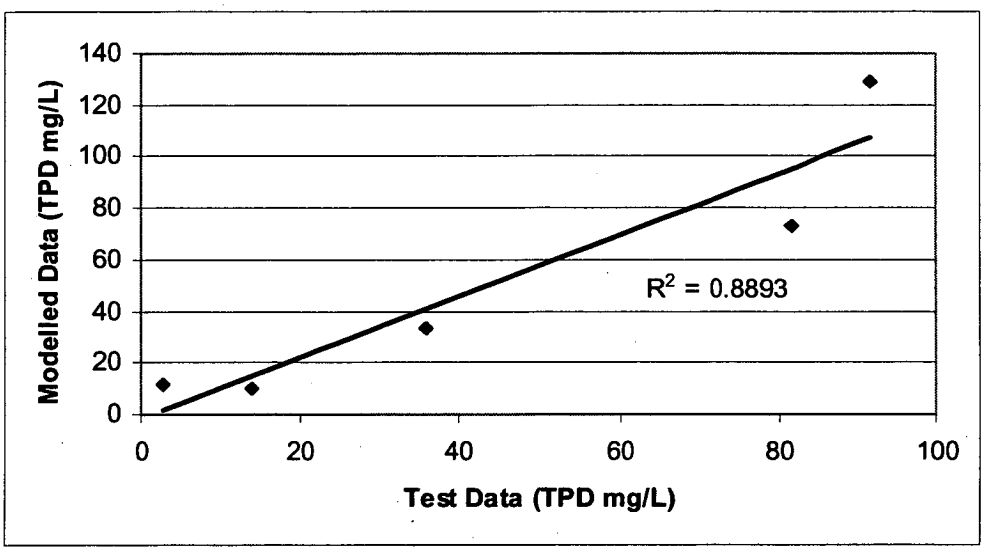


Figure 4.33. X-Y plot of modelled *TPD* of the test data vs. the *TPD* of the test data.

Triangular coordinate contour plot of the model surface

It can be observed, from Figure 4.34, that there is relatively high deposition (>30mg/L) at all compositional mixtures. The first area of high deposition is along the resin acid axis where triglyceride levels are low (<7mg/L). The second area of higher deposition is in the lower right corner of Figure 4.34, where triglyceride levels (>25mg/L) dominate the composition.

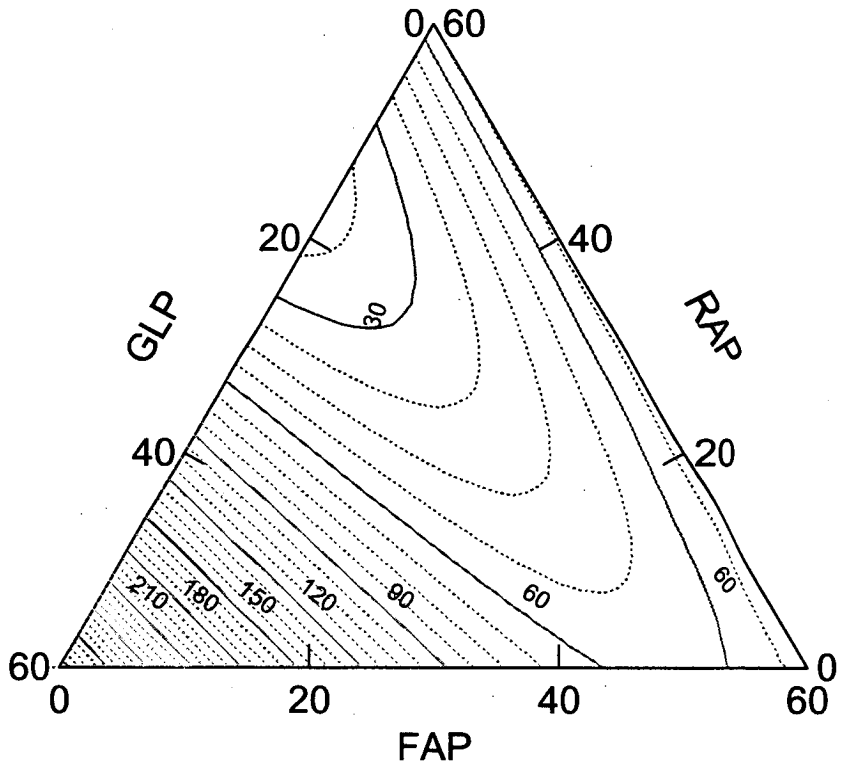


Figure 4.35. Triangular coordinate contour plot of the surface of model 4. (The contour lines indicate modelled *TPD,* all units are in mg/L.)

Raw data, test data and raw modelling results for pH 7.0, 20°C are included in Appendix F.

4.4 Surface Tension

The plotted surfaces of the surface tension data for the pH 7.0, 50°C associated solution concentrations before and after depositions are shown in Figure 4.36 and Figure 4.37 respectively. Both figures show that the surface tension is lowest when the solutions are primarily fatty acid and that the surface tensions are highest when the solution composition is either primarily resin acid or primarily triglyceride.

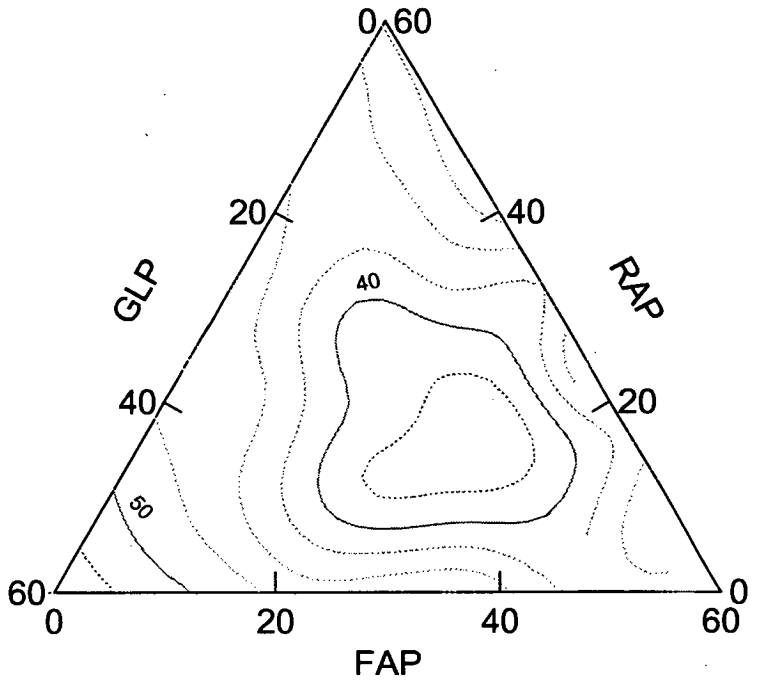


Figure 4.36. Surface tension of pH 7.0, 50°C solutions before deposition.

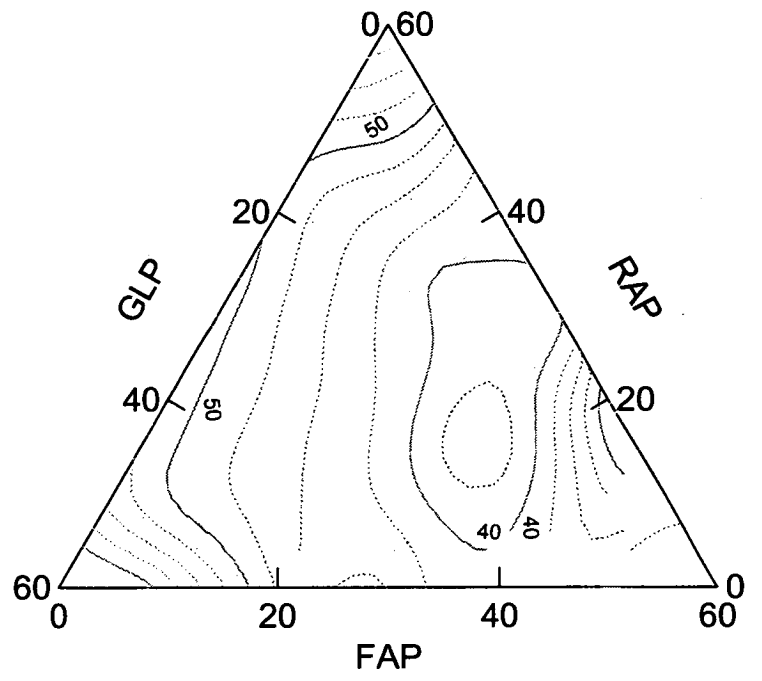


Figure 4.37. Surface tension of pH 7.0, 50°C solutions after deposition.

5. DISCUSSION

Over the course of this chapter the author will attempt to interpret the results obtained in the previous chapter and to place them in context with work reported in the literature.

5.1 Colloidal preparation method

Colloidal dispersions of mixtures of model compounds were prepared by dialysis. Dialysis is a useful laboratory technique in the preparation of industrial representative colloidal wood pitch solutions. It is however more laborious than using a homogeniser[78]. The homogeniser can prepare a colloidal sample within an hour, though up to 85% of the initial pitch components end up deposited on the surfaces of the instrument[78]. Preparing colloidal suspensions by dialysis took over 28 hours but gravimetric/GC analysis showed that, on average, only 25% of the fatty acid , 62% of triglyceride and 81% of resin acid was lost through the process. This is obviously less than from the homogeniser. The particle size of the pitch colloids developed by dialysis[130] and by homogenisation[78] were both representative of size of colloids found in industrial process waters[59].

Since this work made use of purchased model compounds the decision was made to use the dialysis method. Using these approximate dialysis losses, it was relatively easy to target any desired ratio of the three model components in the model pitch solutions.

5.2 Extraction method

A variety of solvents (*t*-BME [46] and DCM [50]) have been used for liquid-liquid extraction of pitch components from water solutions. The key points of interest in the selection of a solvent were safety, cost and effectiveness. *t*-BME provided the best combination of these three factors. Supporting this decision was the fact that the *t*-BME extraction method was used by Örså and Holmbom[46], and has since been used by many others[39, 51, 92, 147, 148]

The variation in data due to extraction, as described in the results section Table 3.8,

shows that less than seven percent error is introduced to the component concentrations due to extraction. A more in depth study into extraction methods might highlight which extraction steps are most influential on this variation. For the purposes of this work the variation levels were acceptable as reproducible data was easily achieved.

5.3 Derivatisation method

The two main derivatisation methods used in the literature are methylation and silylation. Several researchers including Örså and Holmbom [46], Thurbide and Hughes [49], Corin *et al* [51] and Wallis and Wearne [50] have used silylation. Whereas Wearing *et al* [149], Ekman and Holmbom [150], Stack *et al* [24] and others have used methylation.

Methylation is the less expensive of the two methods, although it involves a few more steps due to the preparation of diazomethane. Silylation also has additional advantages in that it allows for the resolution, on this column, of all of the resin acids and it enables the analysis of lignans and free sterols[46]. It was decided to pursue silylation as the means by which to derivatise the pitch extractives.

Silylation is the addition of trimethylsilyl ($-Si(CH_3)_3$) groups to a compound (analyte) in order to increase its volatility[151]. This increased volatility leads to more narrow peaks on gas chromatograms, which in turn allows for easier distinction between compounds (analytes).

The trimethylsilyl ($-Si(CH_3)_3$) group is added to the compound (analyte) by replacing the active hydrogen atom in the following groups (-OH, $-NH_2$, NHR, SH) as follows:

$$ROH + (CH_3)_3SiX \rightarrow ROSi(CH_3)_3 + HX$$

Reaction 5.1.

Various silylating agents are available. The reactivity of the silylating agents is in the following order:

TSIM>BSTFA>BSA>MSTF>TMSDMA>TMSDEA>TMCS>HMDS

TSIM = trimethylsilylimidazole

BSTFA = N,O-bis(trimethylsilyl)trifluoroacetamide

BSA = N,O-bis(trimethylsilyl)-acetamide

MSTFA = N-Methyl-trimethylsilyltrifluoroacetamide

TMSDMA = Trimethylsilyldimethylamine

TMSDEA = Trimethylsilyldiethylamine

TMCS = trimethylchlorosilane

HMDS = Hexamethyldisilazane

In general, the ease of reaction is as follows:

alcohols>phenols>carboxylic acids>amines>amides

BSTFA[46, 50, 51] or BSA[49] have been used as silylation reagents and TCMS or pyridine as silylating aids in the analysis of pulp and paper wood extractives. BSTFA is more reactive as a silylation reagent than BSA[151]. Pyridine is used to absorb acid by-products of silylation whereas the TCMS, a silylation reagent in its own right, was used as an acid catalyst in order to increase the speed of the silylation reaction[151].

The silylation method developed for this project was based on an evaluation of six methods shown in Table 4.8. These methods were based on ones reported in the literature review section. The BSA/pyridine methods had only slightly better performance than the other methods. BSA/pyridine was also the least expensive of the methods evaluated. The combination of cost and performance lead to the selection of BSA/pyridine being the silylation method of choice.

One potential problem encountered with this method of silylation was the co-elution of pimaric and stearic acids (Figure 5.1). As stearic acid was not used in this study this co-elution problem was not an issue.

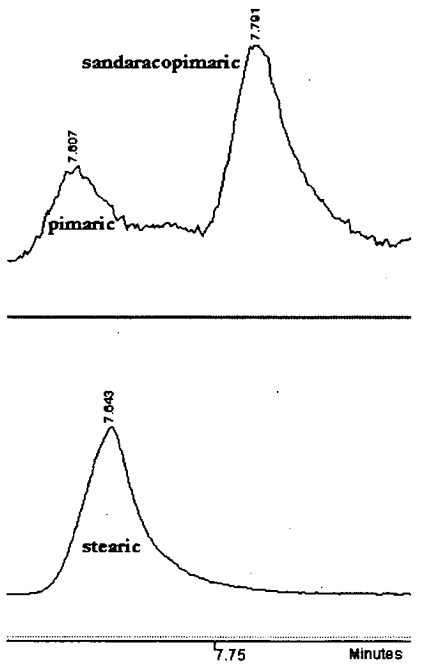


Figure 5.1. Chromatograms of silylated samples of stearic, pimaric and sandaracopimaric acids.

If stearic and pimaric acids were used in a model study, one would have to make changes in order to prevent their co-elution. The key feature of the short column (15m) wide bore (0.53μm) on-column injection method is the ability to analyse fatty acids, resin acids and triglycerides in one run. If further resolution is needed (i.e. stearic and pimaric acids) consideration would have to be given to using either a longer and/or narrower column as well as using a different derivatisation method. Altering parameters of the GC method (e.g. temperatures, temperature ramps, column lengths, carrier gas flows, etc.) might, however, allow for the separation of peaks. One might also consider using the techniques as outlined by Fernandez *et al*[148], where they showed it was possible to analyse underivatised wood extractives. Silylation decreases the polarity of the fatty acids and hence their elution times. With these new elution times it is possible that the pimaric and stearic acids would no longer co-elute. If Fernandez *et al*[148] methods did not provide sufficient separation of peaks one may consider using newly designed high temperature wide bore columns that have a small degree of polarity (ZB-5), as did Thurbide and Hughes[49], such that fatty acids, resin acids and triglycerides could still be measured in one run.

5.4 GC analysis method

Once a suitable GC analysis method was found, little work was done to improve upon it. This project looked at simple mixtures; therefore reliable quantification of the three analytes used in this study was achieved. The short column (15m) analysis method also reduced the analysis time, as compared to longer column methods.

Of the three components analysed it was found that the triglyceride gave the highest variation (i.e. 3.4%), and hence experimental error, in the results. The high triglyceride level injection variations are most likely due to the broad triglyceride chromatograph peak, as seen in Figure 3.4 and Figure 5.3. Future work to improve the GC method should include the exploration of shorter column length as described by Gutiérrez *et al*[152]. Their work showed that improvements in narrowing triglyceride peak widths could be achieved by reduced column length, though possibly at the expense of widening fatty and resin acid peak widths.

Two of the four deposition models were based on data collected from work done by Stack *et al*[24] in which a similar GC analysis method had been used in order to effectively analyse their methylated samples. The deposition data gathered from work by the author and by Stack *et al*[24] can confidently be compared to each other as they were both rigorous in their use of internal standards and checks.

5.5 Deposition and statistical modelling methods

One of the aims of this study was to determine if the interactions between components affected pitch deposition. Mixture models[142] have effectively been used to study chemical interactions, but unfortunately these mixture models require that the total amount of the components used adds up to a constant. Extreme vertices models[143], however, allow for the use of the interaction aspects of mixture models in cases where the sums of the components does not necessarily add up to a constant. An attempt was made to make the extremes, of each component concentration, at a distance that allowed for orthogonal composition design analysis[153]. As creating these distances between extreme component concentrations was not achievable, methods of nonorthogonal general linear regression[134], based on mixture models, were used to determine whether interactions between the pitch components led to the

deposition of pitch. If interactions did occur then they would be identified using pseudo four-dimensional surface interaction plotting techniques[154].

When attempting to statistically model any data set, one must be aware that models, by nature, introduce error in their attempt to estimate. It is therefore important to rigorously explore and test models as encouraged by McLean and Anderson[143]. If this rigorously testing of models isn't undertaken then one may end up comparing modelling techniques rather than the actual models developed.

Though the modelling techniques and the subsequent testing of the models are both sound, one needs to remember that a model only represents the data that was used to create it. The models developed in this work, represent very specific concentrations of only three of the many scores of extractive components. The data was also collected in the absence of fines, fibre, and other substances common to the waters of papermaking. The data was collected under conditions of constant temperature, pH and shear rates. Industrial papermaking waters however may contain many more variables and even fewer constant conditions. Nevertheless the models developed should provide a useful starting point for understanding what happens in the industrial situation.

The pHs, temperatures and shear rates evaluated are representative of papermaking conditions. The three extractive components (i.e. oleic acid, abietic acid and triolein) of the model pitch solutions (i.e. *FAP*, *RAP* and *GLP*) were selected as they are common extractives found in *Pinus radiata*[53] as well as in a range of pulpwoods[155].

The fatty acid (oleic acid, 99+% purity) and triglyceride (triolein, 99% purity) used in this study were relatively pure, whereas the resin acid (abietic acid) was of technical grade (labelled 70% purity) and contained a range of resin acids and other impurities as shown in Figure 5.2. as determined by using pure resin acid samples and the analytical techniques described in the Methods section. The actual abietic acid in the technical grade sample was found to be 54.4 percent abietic acid based on the total analysed area of the chromatogram. This percentage represents 70% of the resin acid content. The total resin acid concentration of the technical grade abietic acid was 77.7%. The range of resin acids helps to better model industrial papermaking conditions, though it does restrict the discussion of the results to resin

acids in general, rather than specific classes of resin acids.

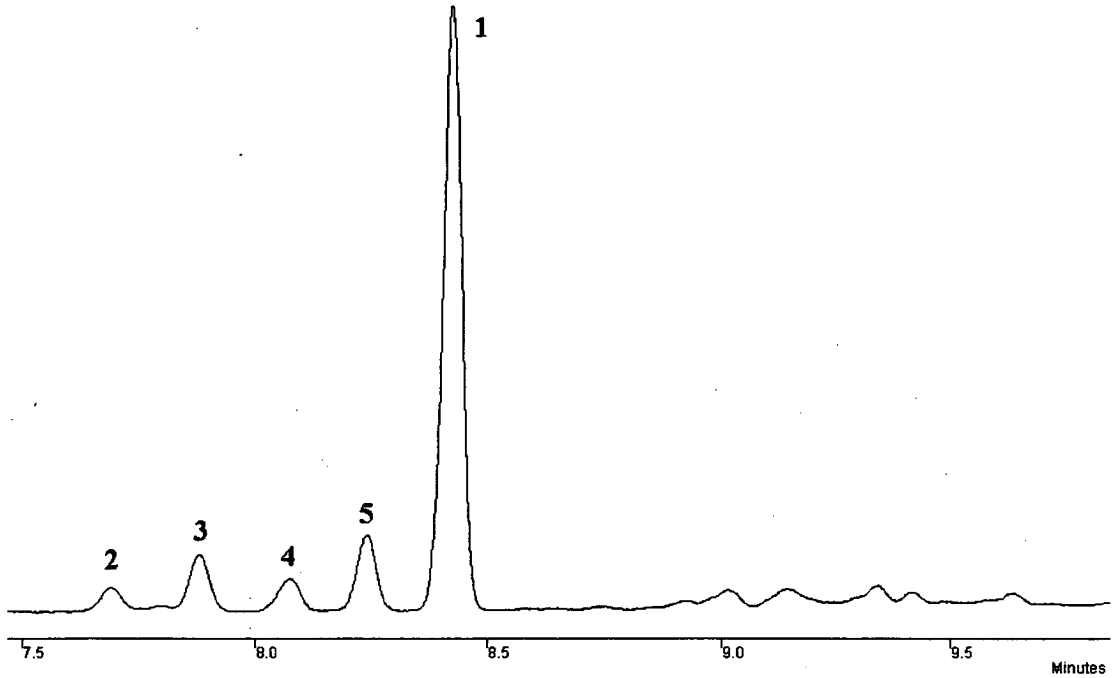


Figure 5.2. Chromatogram of the silylated technical grade abietic acid. (**1** abietic acid (54.4%), **2** pimaric acid (2.7%), **3** isopimaric acid (6.1%), **4** palustric acid (5.4%) and **5** dehydroabietic acid (9.1%))

The deposition modelling shows that different pitch deposition behaviour occurs at different temperatures and pHs. This reaffirms the variability in deposition tendencies, due to temperature and pH, which was found by Dreisbach and Michalopoulos[55] and Hassler[16].

The final statistical models developed to explain pitch depositions at various temperatures and pHs explored by the author and by Stack *et al*[24] are listed in Table 5.1 along with some of the statistical tests performed on the models.

From Table 5.1 one notes that though the deposition model for pH 7.0, 50°C is statistically sound and significant, it is not as robust as the other models are in their ability to estimate depositions. It is believed that this is due to two main factors. First of which were difficulties in measuring pH as the pH approached 7. This was due to the rapid fouling of the pH probe. Difficulties in regards to pH measurement are further detailed in Appendix A. Secondly, some triglyceride hydrolysis to fatty acid was observed, as shown in Figure 5.3 by the appearance of fatty acid (peak **8**) after the deposition of a mixture of triglyceride and resin acid.

Table 5.1. Summary of model regressors, fit and test statistics for the final models selected for each of the pH and temperature conditions. (** using data from experiments conducted by Stack *et al* [24].

pH	5.5 **	7.0	5.5	7.0 **
°C	20	50	50	20
Model #	3	5	4	4
β_0	12.865	3.710		
β_1		0.247	0.363	1.192
β_2			0.708	1.123
β_3			0.110	-1.276
β_4	0.041		-0.010	
β_5	-0.023	-0.014	-0.008	
β_6	0.013	-0.009		-0.052
β_7	-0.018		0.006	
β_8	-0.003	0.017		
β_9		0.011		0.107
R^2	0.862	0.587	0.846	0.937
R_A^2	0.850	0.549	0.89	0.921
F-ratio	67.610	15.355	115.761	59.547
Test 2 R^2	0.8623	0.5871	0.8469	0.938
Test 3 R^2	0.852	0.221	0.9218	0.8893

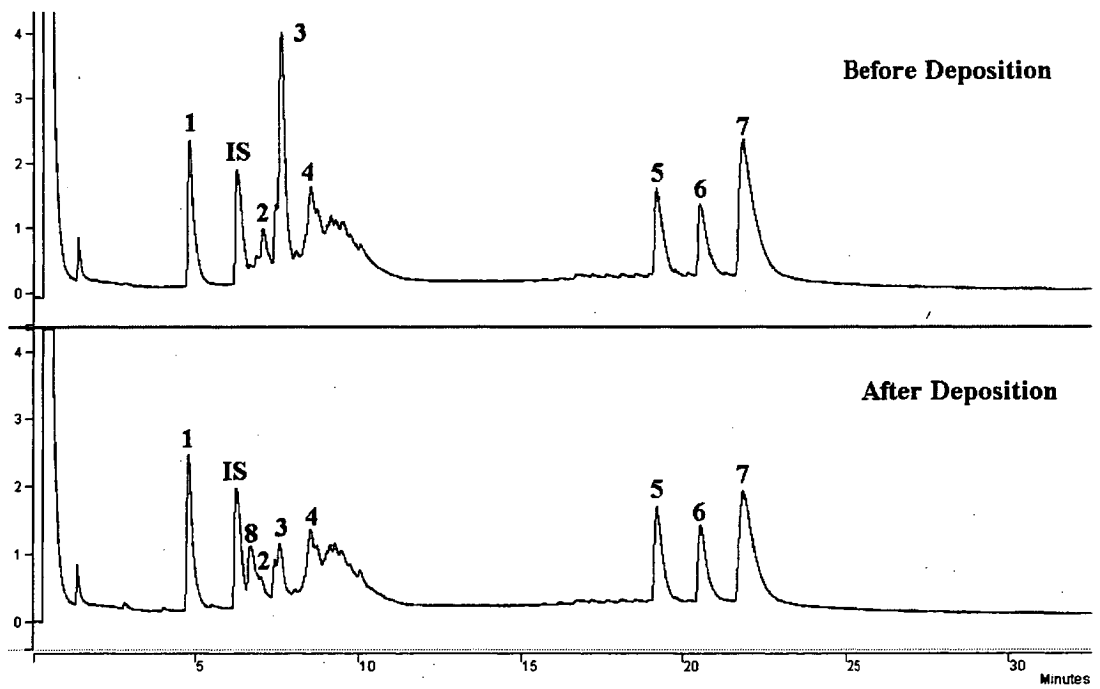


Figure 5.3. Chromatograms of a sample of triglyceride before and after deposition, showing the hydrolysis of triolein to fatty acids. (**1** pentadecanoic acid, **IS** heptadecanoic acid, **2** isopimaric acid, **3** abietic acid, **4** neoabietic acid, **5** cholesteryl stearate, **6** DOG, **7** triolein, **8** fatty acid C18:x)

This hydrolysis is believed to be due to localised high KOH concentrations (~3.56M)

whilst adjusting the deposition solution from pH 5.0 to pH 7.0. In adjusting the pH from 5.0 to 5.5 a 0.18M KOH solution was used, where as in adjusting from pH 5.0 to 7.0 a 3.56M KOH solution was used. Although some 40-80 drops of this lower concentration KOH would have been required to adjust the pH from 5.0 to 7.0 in retrospect this should have been done.

The data developed by Stack *et al*[24] did not target single and dual component compositions. This is graphically explained in Figure 5.4 where Figures 5.4b and 5.4d have no data points along any of the three axes. The absence of single and dual component data does not make the statistical modelling invalid. It does however limit the range of component concentrations where the model is valid. The absence of single and dual component mixtures also reduces the robust prediction of component interactions.

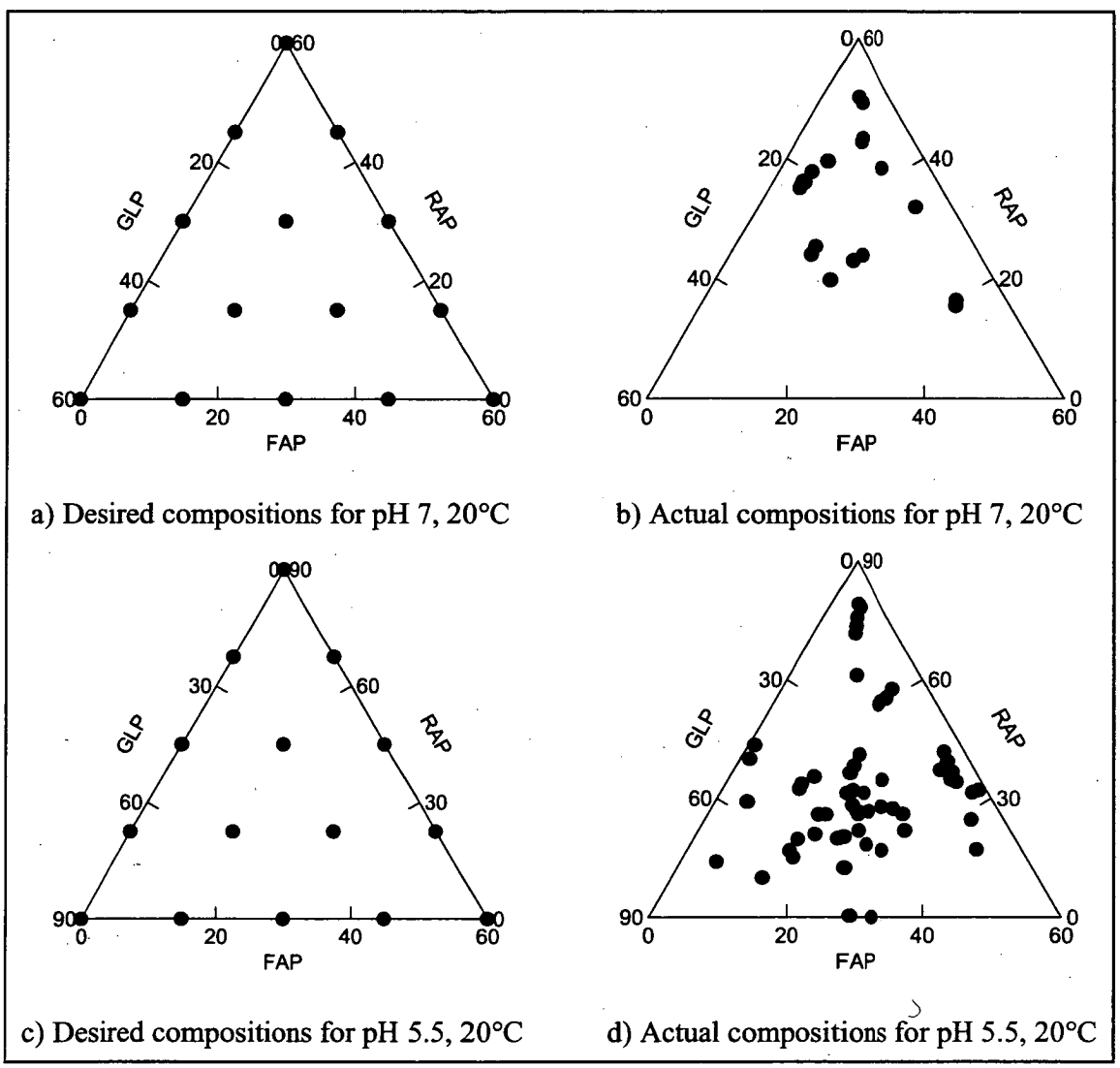


Figure 5.4. Ideal mixture model data sets compared to actual data sets from the work by Stack *et al* [24].

5.6 Visualisation of deposition surfaces

The decision to use two-dimensional triangular coordinate contour plots, to display the four dimensions of data, was made knowing the difficulties associated with interpreting this type of graphical plot. Yu and Stockford[156] made a strong case when they said that it can be confusing and even misleading for humans living in a three dimensional world reading two dimensional graphs, found in traditional print media, to interpret higher-dimension visualisation techniques depicting more than three dimensions. Wilkinson [157] stated that when viewing statistical graphs readers are vulnerable to visual illusions. Wilkinson [154] later hinted that viewing multiple dimensional data in a two dimensional manner compromises the readers' ability to accurately perceive multivariate relationships.

An investment of time is required, on behalf of the reader, to interpret two-dimensional triangular coordinate contour plots of four- dimensional data. This investment in time is rewarded by the ability to quickly and easily identify interactions within a four dimensional system.

The first step is to properly identify the concentration of each of the three components, leading to deposition, at any point within the triangular coordinate plot. All three sides of the triangle in Figure 5.5 are labelled according to the extractive they represent (*RAP*, *FAP* or *GLP*). In reading the coordinates for any point within the triangular plot, one draws a line perpendicular to the plane of increasing component concentration to the label axis. The example given in Figure 5.5 is the point that represents 35mg/L of *FAP*, 20mg/L of *GLP* and 5mg/L of *RAP*

The second step is determining component interactions by the examination of the shape of the contour lines within a triangular coordinate plot. The amount of total pitch deposited (*TPD* in mg/L) at any given combination of resin acid, fatty acid and triglyceride is recorded on the actual contour lines within the triangular plot. The shapes of these contour lines express the influences, and interactions between components, that the three variables (*FAP*, *RAP* and *GLP*) have on *TPD*.

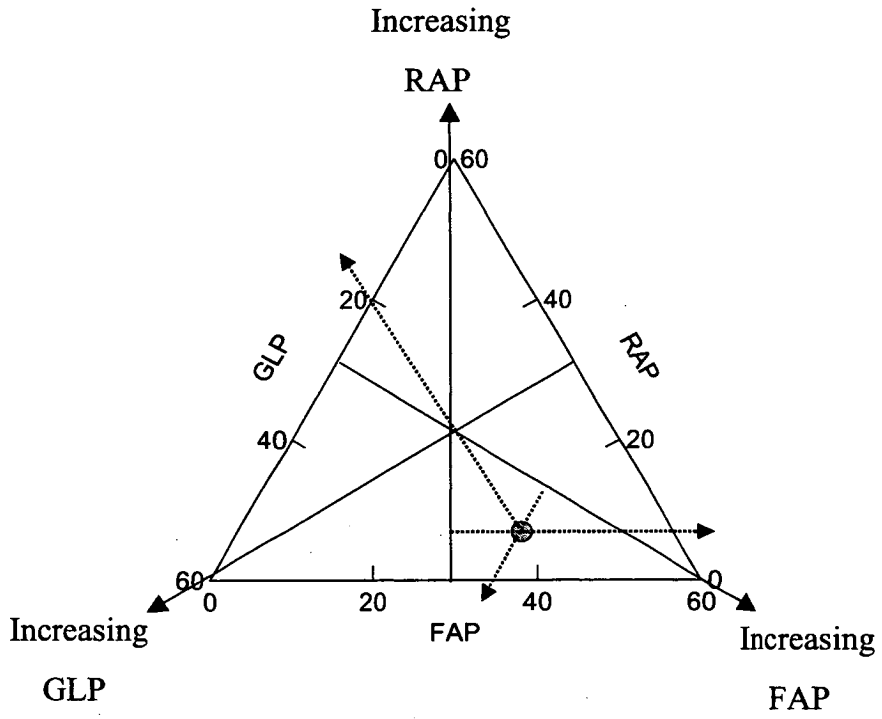


Figure 5.5. Diagram explaining triangular coordinate systems. Illustrating a point of 35mg/L *FAP*, 20mg/L *GLP* and 5mg/L *RAP*.[158]

If only one component is responsible for deposition (*TPD*) (i.e. no interaction between components) then the contour lines will be linear and perpendicular to the concentration plane of the component responsible for deposition. Figure 5.6 is an example of a system where only one component (*RAP*) is responsible for *TPD*. This deposition model is shown in both pseudo 3D (Figure 5.6a) and 2D (Figure 5.6b) to allow for the both visual understanding of the lack of interaction and the interpretative appreciation of the two dimensional triangular coordinate contour plot.

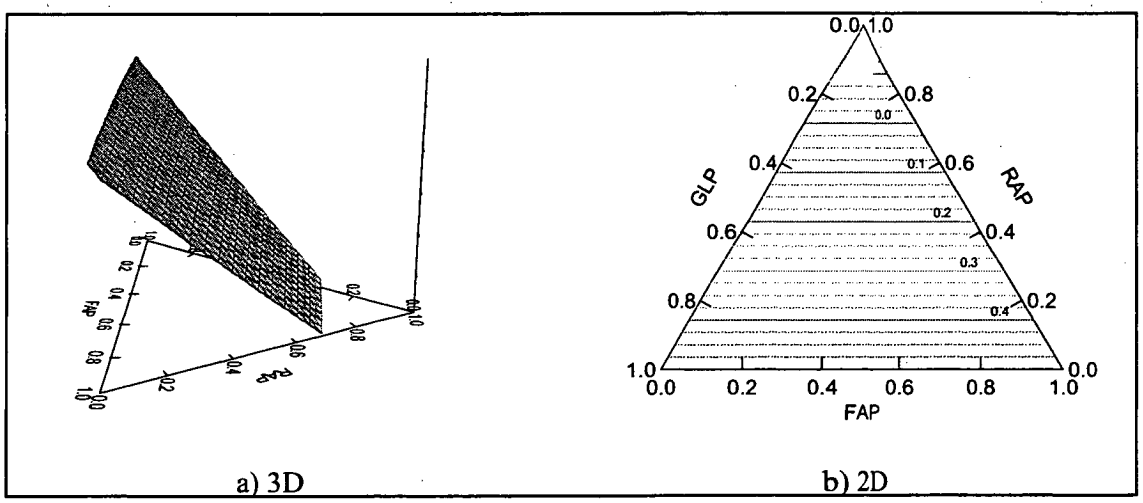


Figure 5.6. 3D Surface plot & 2D contour plot of a system with one component response (*RAP*) and no component interaction.

When the interaction of all three components is responsible for deposition (*TPD*) the contour lines will be circular. Figure 5.7 is an example of a system where the interaction of all three components is responsible for *TPD*.

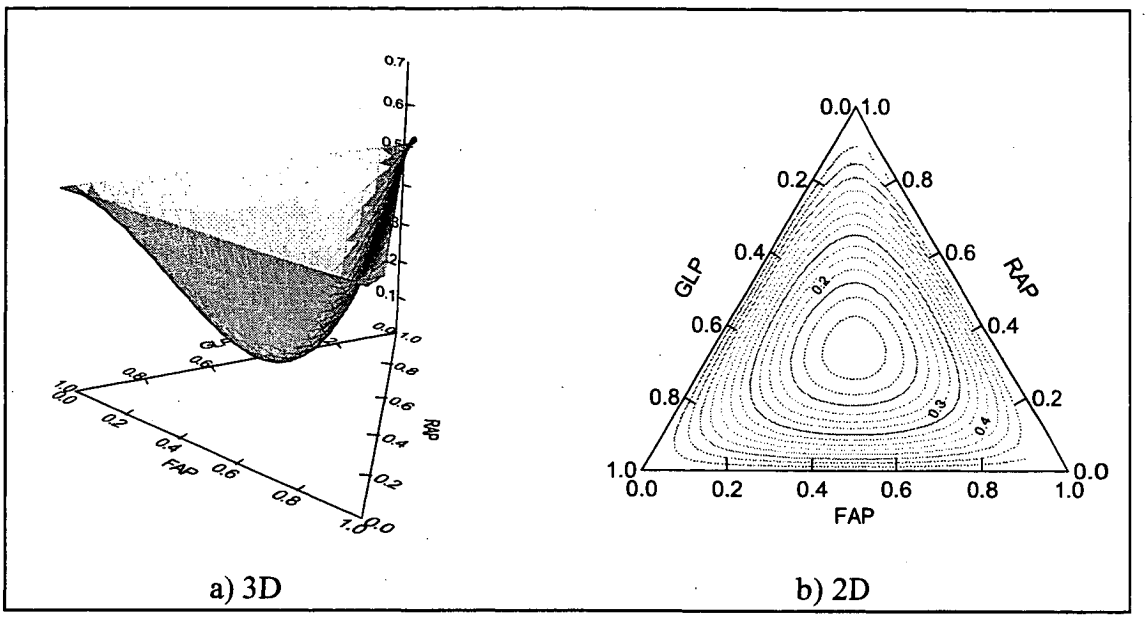


Figure 5.7. 3D Surface plot & 2D contour plot of a system with interaction between three components.

Figures 5.6 and 5.7 highlight the ease of interpreting no interaction and three-way interaction between components using triangular coordinate contour plots. Two-way interactions between components are relatively easy to identify in that the contour lines are parabolic in shape. An example of a two-way interaction between *FAP* and *RAP*, being responsible for *TPD*, is shown in Figure 5.8.

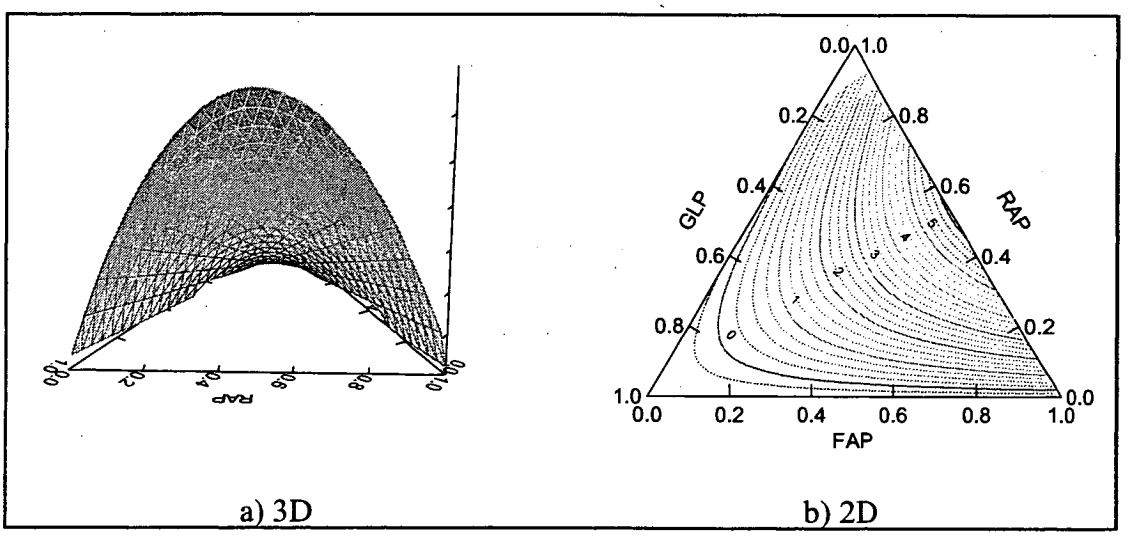


Figure 5.8. 3D Surface plot & 2D contour plot of a system with interaction between two components.

The final step in interpreting triangular coordinate contour plots of two-way interactions is determining which two components are responsible for the two-way interactions easily identified by the parabolic contour lines of deposition. If a line drawn through the parabolic apices is parallel to the concentration plane of one of the three components, then that component is not involved in the two-way interaction. The different two-way interactions are explained graphically in Figure 5.9.

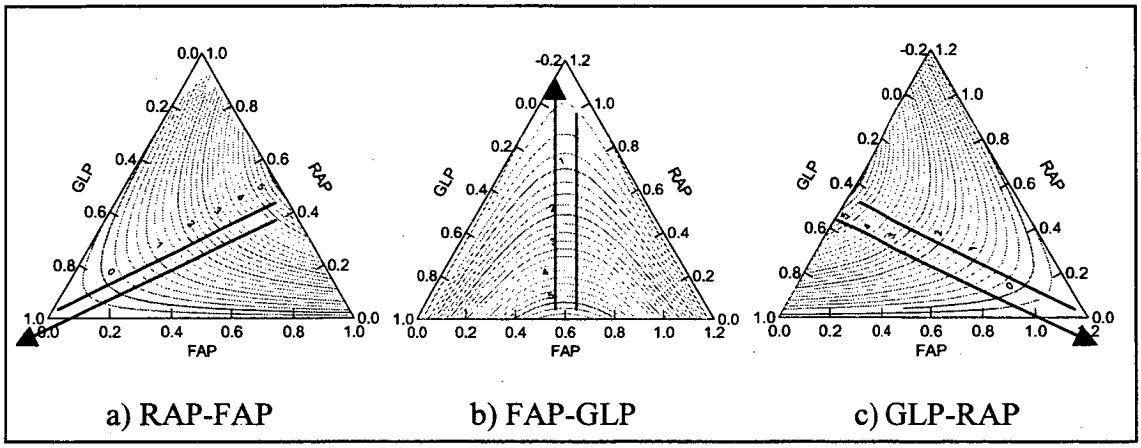


Figure 5.9. Deposition models of two-way interaction between components.

5.7 Deposition surfaces and control strategies

The models developed provide a way to understand the deposition behaviour in terms of three components and the interaction between the components at different levels of pH and temperature experienced on paper machines. The next step is to use these models to determine the best control strategies for the reduction of pitch deposition.

pH 5.5, 50°C

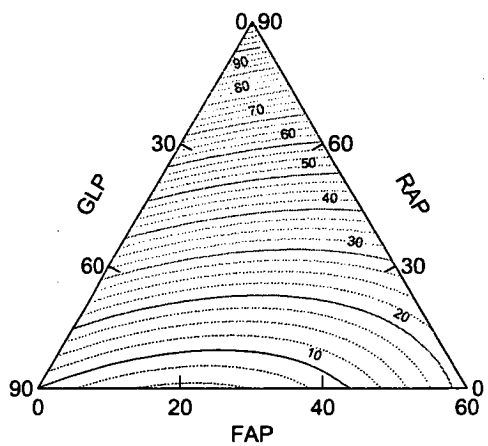


Figure 5.10. Model deposition surface plot for pH 5.5, 50°C.

The surface of the model for the pH 5.5, 50°C deposition data is shown in Figure 5.10. The near linear contour lines, similar to those of Figure 5.6, suggest that there is little interaction between components and that the amount of resin acid present is directly proportional to the amount of pitch deposited. With a system that is driven primarily by one component (e.g. resin acid) control strategies become very simple, all one needs to do is control the component responsible for deposition. Potential control strategies that should be most effective in pH 5.5, 50°C conditions would be ones that are selective towards the fixation of resin acids to fibre and fines. Very little information exists in regards to pitch component specific fixatives. Richardson *et al*[25] have recently presented results, which detail the differences between resin acid and triglyceride fixation using two distinct fixative chemistries. These authors showed that a modified polyethyleneimine chemistry fixed ~80% of the resin acids to the fibre at pH 6, and only ~50% of the triglycerides to the fibre at a dose rate of 1 kg of chemical per tonne of fibre. In contrast a cationic acrylamide copolymer chemistry fixed ~80% of the resin acids to the fibre at pH 6, and ~70% of the triglycerides to the fibre at the same dose rate. The pH 5.5, 50°C deposition model highlights the potential for further work to identify, or develop, component specific fixatives.

pH 5.5, 20°C

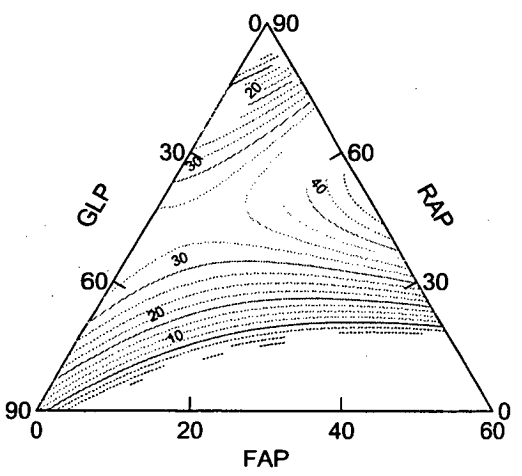
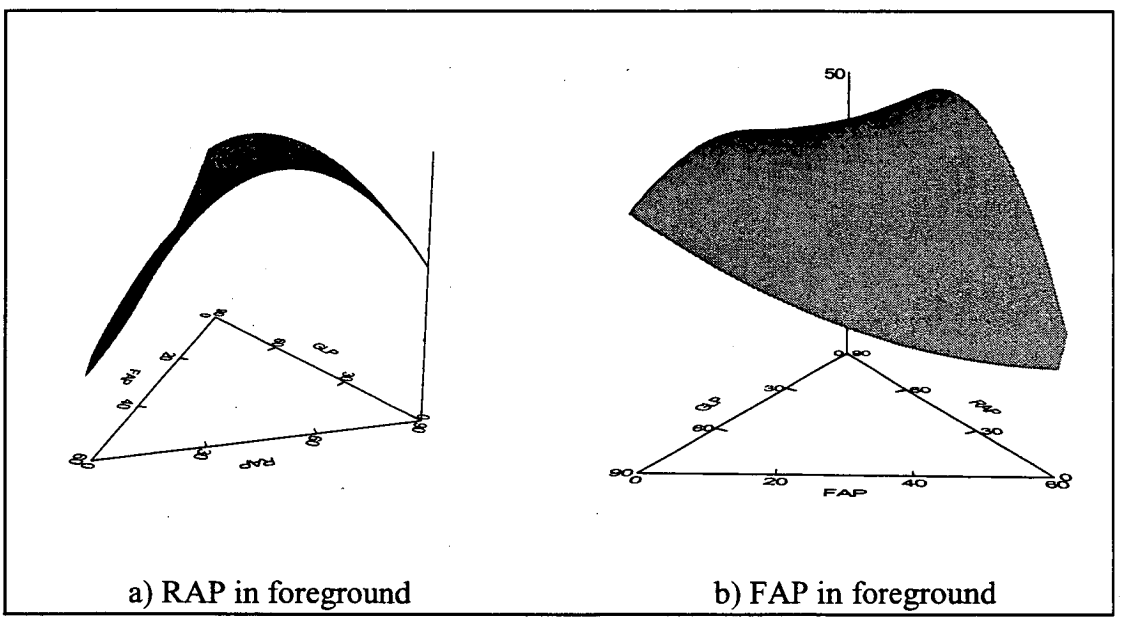


Figure 5.11. Model deposition surface plot for pH 5.5, 20°C.

Examination of the contour lines in Figure 5.11 is challenging in that it does not follow textbook two-way, three-way and no interaction plots as shown in Figures 5.8,

5.7 and 5.6. Initially Figure 5.11 appears to have relatively linear contour lines, then one notices the hump along the resin acid axis and the fact that the values of the contour lines decrease as one moves towards the top and/or bottom of the triangular plot. As a result of these observations the reader then realises that interactions between components are occurring, but determining how many and which components are interacting appears quite challenging. A 3D plot of the deposition model, as shown in Figure 5.12, for these conditions, pH 5.5 and 20°C, helps the reader in his/her ability to see the nature of the interaction(s).



a) RAP in foreground b) FAP in foreground

Figure 5.12. Triangular coordinate 3D surface plot of depositions at pH 5.5, 20°C. (The surface indicates modelled *TPD,* all units are in mg/L.)

The apex of the surface in Figure 5.12a is above the *RAP* axis suggesting that there is a strong interaction between resin and fatty acids. The curvature at the top of the deposition surface in Figure 5.12b, with *FAP* in the foreground, suggests that there is a slight interaction between fatty acid and triglyceride.

Stack *et al*[24] when reporting their results developed a slightly different model. The model they developed which is shown in Table 5.2 was based on a 'mixture model' with no constant term (model 2). Their model included linear terms as well as two-way interaction terms. The magnitude of the regression coefficients (β_4 through β_8) in both models was similar

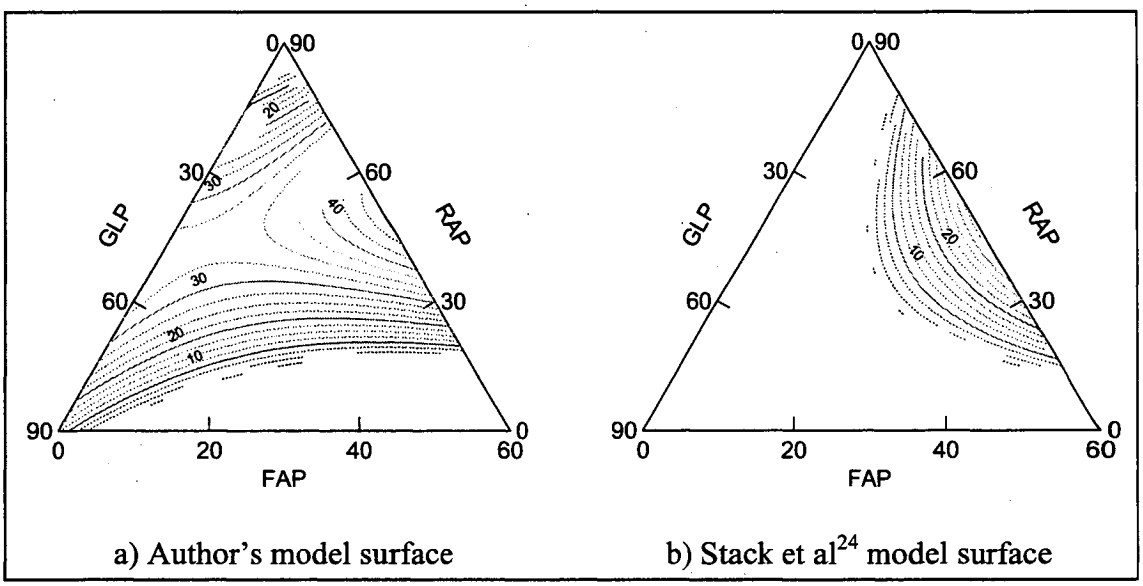
Table 5.2. Summary of model regressors for pH 5.5, 20°C. (** using data from experiments conducted by Stack *et al* [24] .

Model by:	Author**	Stack *et al* [24]
pH	5.5	5.5
°C	20	20
Model #	3	2
β_0	12.865	
β_1		0.570
β_2		0.463
β_3		0.319
β_4	0.041	0.0192
β_5	-0.023	-0.0248
β_6	0.013	-0.0167
β_7	-0.018	-0.0162
β_8	-0.003	-0.0076
β_9		-0.0044
Test 2 R^2	0.8623	0.854

Triangular coordinate contour plots of the two models, shown in Figure 5.13, display similar shape in the region near the *RAP* axis. Stack *et al*[24] explain this interaction behaviour in terms of pitch viscosity modifying agents (PVMA). Both models in Table 5.2 support this theory by highlighting the same areas of high and low pitch deposition. The fact that the contour lines in Figure 5.13a slope in different directions highlights the complexity in predicting pitch deposition at pH 5.5, 20°C. These differences in models may also be attributed to the fact that there is a lack of single and dual component data sets, this is highlighted by the absence of data points along the axes in Figure 5.4d. The contour lines, of the author's model, also indicate that the surface is somewhat responsive to the interactions of the three components, where as this is not shown by the model developed by Stack *et al*[24].

The complexity in predicting pitch deposition also highlights difficulties in selecting appropriate pitch control strategies for pH 5.5, 20°C. Although very few paper machines operate at this temperature many laboratory studies have been conducted at this (i.e. room) temperature. This temperature is also a common utility water temperature and therefore a very likely temperature that may mix with higher temperature paper machine process waters. This localised mixing of high and low temperature waters is commonly referred to as a "temperature shock". In a system of pH 5.5, 20°C control strategies that equally fixed resin and fatty acids would reduce pitch deposition but not necessarily stop deposition. The area of highest contour

lines values (TPD) is within the mixing, or interaction, area of fatty and resin acids. The fact that the highest depositions are within this area of interaction highlights that one would have to stop the interaction between these components in order to stop deposition. This could help to explain why chemistries (e.g. talc[159] and other detackifying chemistries[109, 110]) which are meant to hamper, or prohibit, the interactions between pitch extractive components tend to be more effective at lower pH and temperatures[107, 160]. It is believed that talc coats pitch particles and as such prevents their interaction[159].



a) Author's model surface b) Stack et al[24] model surface

Figure 5.13. Triangular coordinate contour plot of the surface of the model developed for pH 5.5, 20°C using data from Stack *et al* [24]. (The contour lines indicate modelled *TPD,* all units are in mg/L.)

pH 7.0, 50°C

The original modelled deposition surface for pH 7.0, 50°C shown in Figure 5.14a was plotted with extended *GLP* and *RAP* axes in order to allow easier comparisons between the pH 5.5 and pH 7.0 studies. The extended axes model of pH 7.0, 50°C is shown in Figure 5.14b. By extending these axes, however deposition surfaces are shown in areas where the model cannot confidently predict. The maximum levels of *FAP*(60mg/L), *GLP*(38mg/L) and *RAP*(60mg/L) that the model is able to confidently predict, as determined by the experimental data sets, are shown in Figure 5.15. As a result of these maximum levels of extractives Figure 5.14c has the areas where the model loses confidence shaded over.

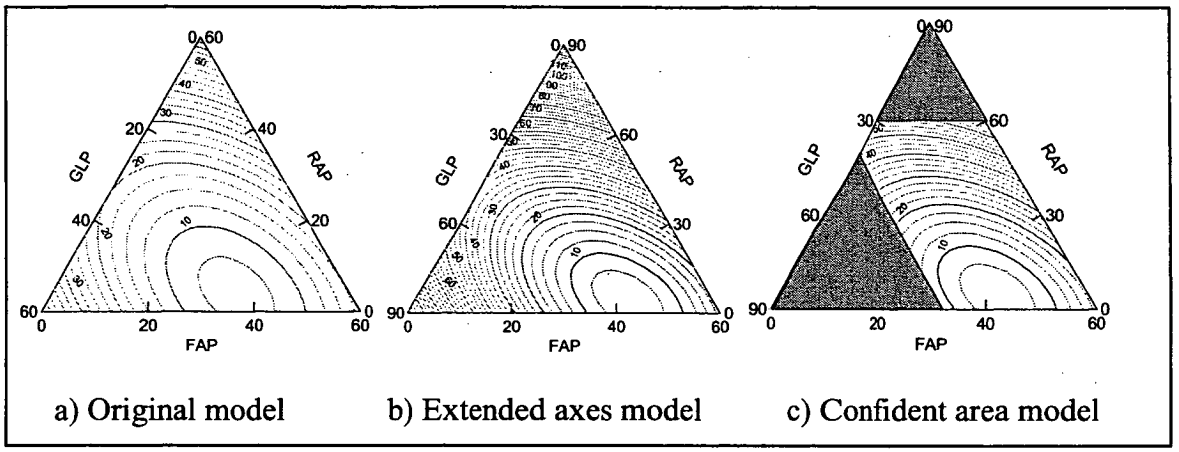


Figure 5.14. Model deposition surface plots for pH 7.0, 50°C.

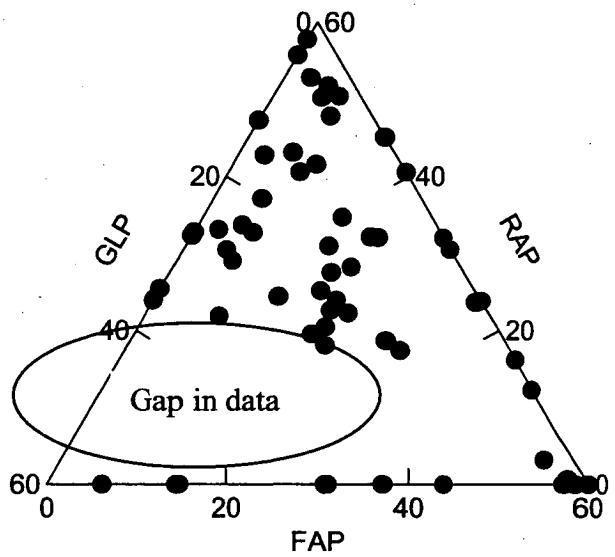


Figure 5.15. Deposition data pH 7.0, 50°C

The circular shape of the contour lines in Figure 5.14c suggests the possibility that all three components are interacting, as in Figure 5.7. The near parabolic shape of the contour lines in Figure 5.14c suggests that if the three components are interacting that the interaction is primarily between *GLP* and *RAP* as shown in Figure 5.9c. A decrease in *GLP* or *RAP* concentrations would lead to reduced deposition. From a control strategy standpoint this could be accomplished in two ways. Firstly, by fixation of both the *GLP* and *RAP* to the fines and fibres. Richardson *et al*[25] highlighted the fact that some fixatives are better able to bind both GLP and RAP to the fibres than other fixatives. If a fixative was only able to bind one of the two components then increased deposition could occur. Further work would be helpful in aiding the proper selection of fixatives for the specific needs of the variety of

papermaking system chemistries. A second way to reduce deposition at pH 7.0, 50°C would be to increase *FAP* concentrations. One potential way of doing this is through the enzymatic hydrolysis of a triglyceride molecule into three fatty acid molecules and one glycerol molecule, as described by Chen *et al*[96]. This highlights a biological pitch control method described in section 2.4.

The advantage of converting the triglycerides to fatty acids may only be a seasonal benefit as the large triglyceride concentrations available for hydrolysis are more prevalent in winter than in summer[23, 24].

pH 7.0, 20°C

In order to allow for the easy comparison between deposition surfaces the original deposition surface for pH 7.0, 20°C shown in Figure 5.16a had its axes modified as shown in Figure 5.16b. These modifications extend the model into concentrations where it cannot confidently predict depositions. Areas where the model loses confidence, as defined by Figure 5.17, were shaded over as shown in Figure 5.16c.

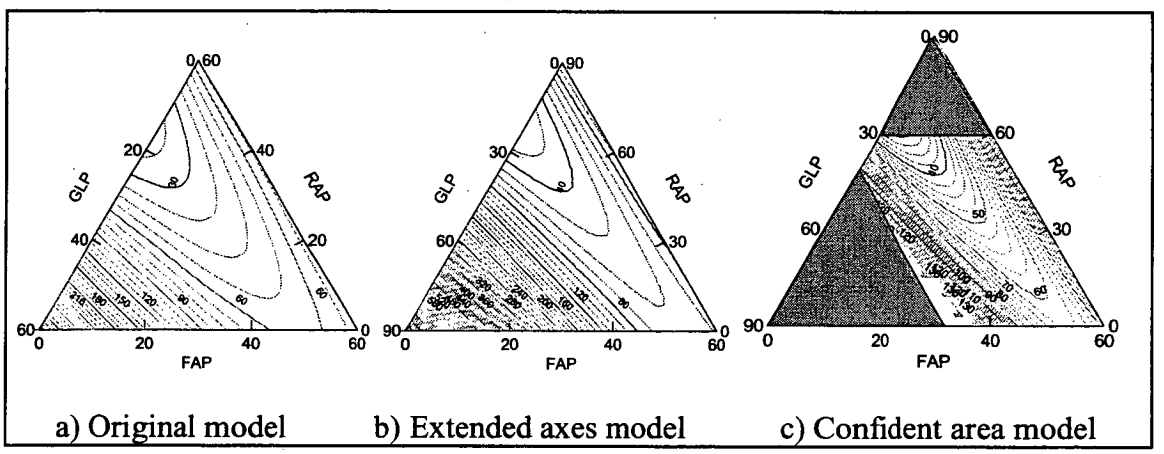


Figure 5.16. Model deposition surface plots for pH 7.0, 20°C.

The parabolic contour lines of Figure 5.16c suggest that there is an interaction between *GLP* and *RAP* and that it is this interaction that influences deposition as shown in Figure 5.9c. Figure 5.16c illustrates a set of temperature and pH conditions wherein control strategies for the reduction of pitch deposition are not straightforward. Fortunately these conditions of temperature and pH are not common to papermaking systems, these conditions are however relatively common

for pulp and paper mill effluent treatment. A shock cooling from pH 7.0, 50°C to 20°C would result in an increase in pitch deposition and as such should be avoided.

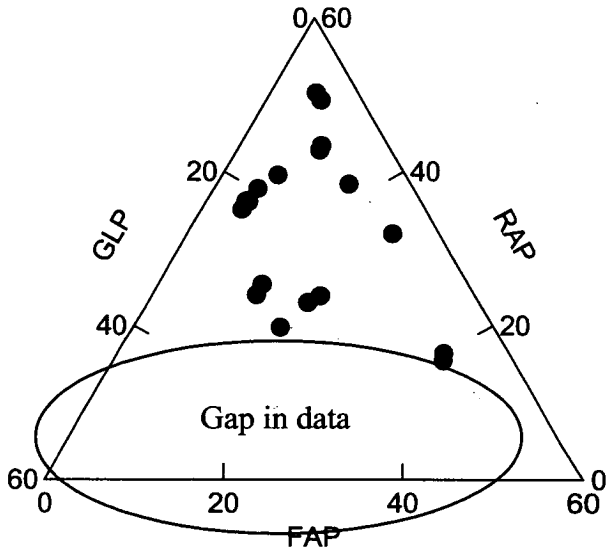


Figure 5.17. Deposition data pH 7.0, 20°C

5.8 Comparison of deposition surfaces

In order to explain the effect of pH and temperature on deposition, the final deposition surface model for each of the temperature and pH conditions has been assembled in Figure 5.18. The deposition behaviour in the graphs show very different behaviour for the four conditions of pH and temperature investigated. As a result significant changes in deposition could occur due to pH and temperature shocks.

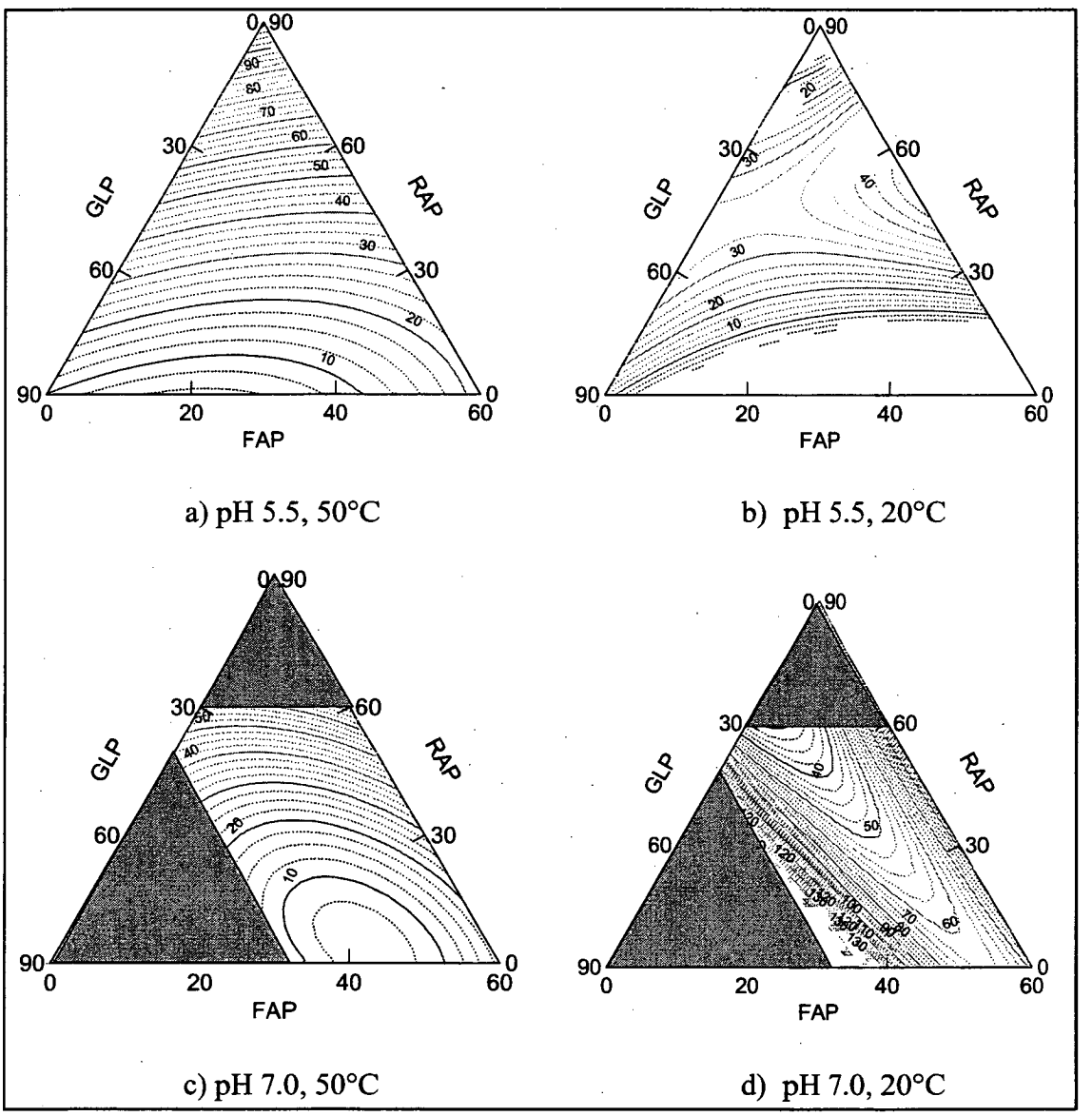


Figure 5.18. Model surface plots for each of the pH and temperature conditions.

There are compositions however where a temperature and or pH shock would have little or no effect on deposition. Overlaying Figures 5.18a, 5.18b, 5.18c and 5.18d shows only one point of common deposition (i.e. the *TPD* is the same for all four

systems and is ~42 mg/L). This point of common deposition is where the pre-deposition triglyceride to fatty acid to resin acid molar ratio is 1:4:11. The overlap of all four pH and temperature conditions is shown in Figure 5.19.

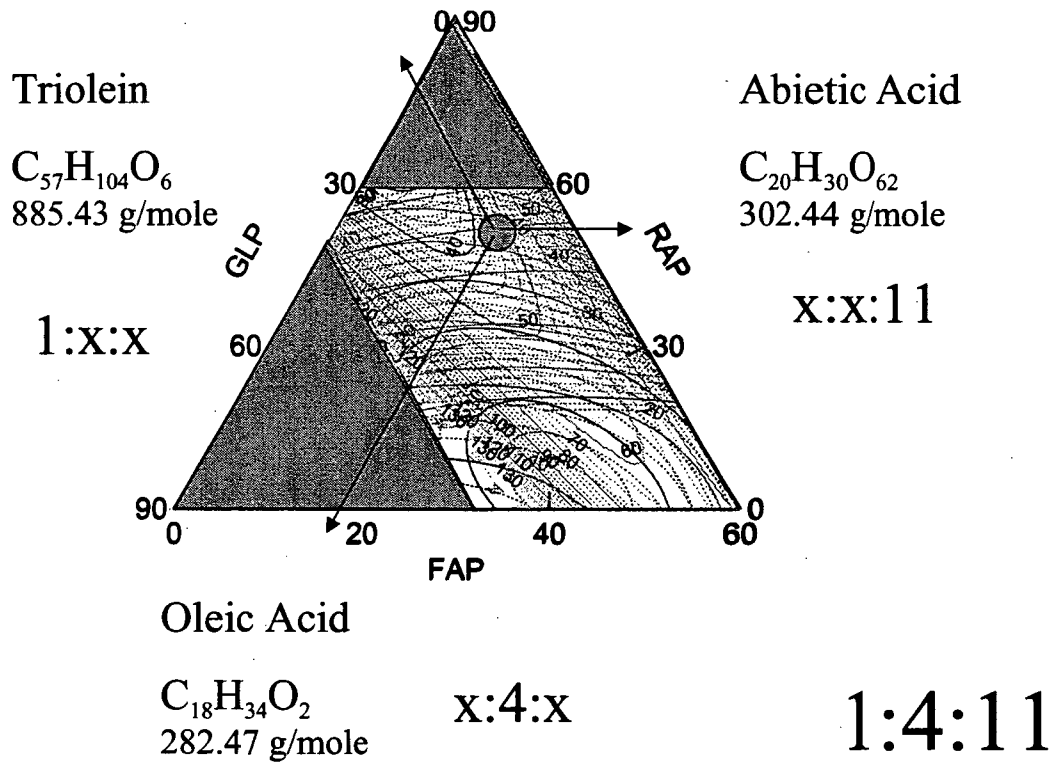


Figure 5.19. Point of common deposition and stoichiometry for all temperature and pH conditions. (1 mole Triolein, 4 moles Oleic acid, 11 moles Abietic acid)

The existence of a point, at any pH and temperature, where deposition is the same and that the components involved are in a set molar ratio suggests that the interaction between the components are stoichiometric in nature. This stoichiometric relationship may suggest that chemical interactions leads to deposition, though more plausibly due to the hydrogen bonding of extractive components as described by Vercoe *et al*[161]. In either case the stoichiometric interactions suggest that something in addition to, or other than, physical parameters such as particle size and viscosity are at work.

In order to explain the differences in deposition behaviour that arise due to temperature and pH one needs to consider the effect that these variables have on the chemical and physical properties of a system. It is known that pH will affect the

chemical nature of the compounds and hence the interaction between them.

If hydrogen bonding interactions are occurring, these interactions can only be occurring in solution. An example of the hydrogen bonding between carboxylic acids (i.e. oleic and abietic acid) is shown in Figure 5.20.

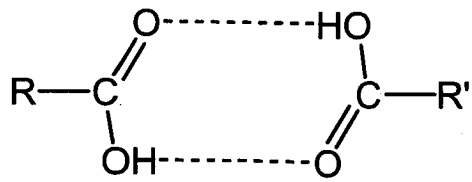


Figure 5.20. Hydrogen bonding (i.e. dimer) interaction between carboxylic acids[162]

Solubilities of the abietic acid and oleic acid can be found in literature in the form of pK_a values. These are shown in Table 5.3.

Table 5.3. Summary of component pKa's at 20°C.

Component	pK_a
Oleic Acid	9.85[57]
Abietic Acid	6.4[58]
Triolein	Not applicable

At pHs below the pK_a, resin and fatty acids are found in their undissociated state. In the undissociated form these acids have low solubility[163]. At pHs above the pK_a, resin and fatty acids are found in their ionised form according to Reaction 5.2.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

Reaction 5.2.

Suckling *et al*[56] were able to determine solubilities of fatty acids, resin acids and triglycerides by measuring the percentage of components soluble in water of varying pH. Figure 5.21 is an excerpt from the paper by Suckling *et al*[56].

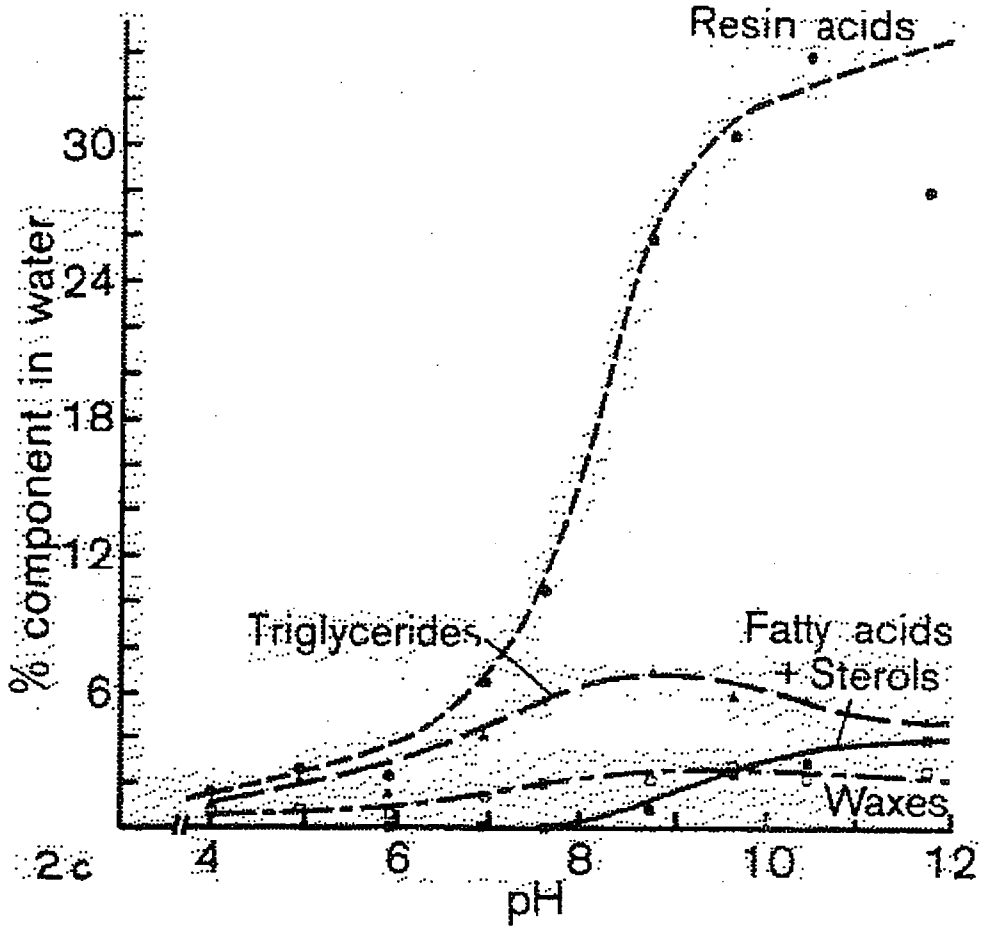


Figure 5.21. pH effect on the dissolution of extractive components, from Suckling *et al*[56].

From Figure 5.21 one can observe that for an increase from a pH of 5.5 to a pH of 7.0 more *RAP* and *GLP* would become soluble and that the amount of soluble *FAP* would remain the same. This increase in solubility of *RAP* and *GLP* can help to explain why at pH 7.0 the deposition surface models are of interactions between *RAP* and *GLP*, as seen in Figures 5.18c and 5.18d. Interactions between molecules can only occur when they are in solution. Increasing pH, however, decreases the likelihood of hydrogen bonding because the acidic proton of the carboxylic acids is more dissociated at higher pHs, as shown in Reaction 5.3.

$$RCOOH + OH^- \rightarrow RCOO^- + H_2O$$

Reaction 5.3.

Increasing the degree of dissociation of carboxylic acid group of resin acid at pH 7 should result in a decrease in the likelihood of hydrogen bonding occurring between

dissociated molecules. However, when pH (e.g. 7.0) is close to the pK_a (e.g. 6.4) there still exists a large amount (i.e. ~50%) undissociated carboxylic acid groups. In addition there are ion-dipole interactions between dissociated and undissociated carboxylic acids, as shown in Figure 5.22. These ion-dipole interactions may also be responsible for pitch deposition.

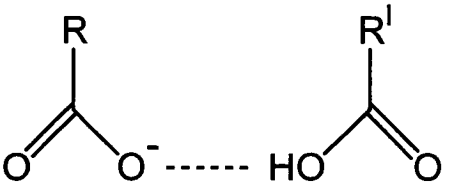


Figure 5.22. Ion-dipole interaction between two carboxylic acids (maximum when $pH \approx pK_a$)[57]

If the deposition and interaction of pitch can be explained by the amount of pitch in solution at different pHs, how can deposition and interaction be explained at different temperatures? Understanding of temperature effects on deposition appears to be more difficult than understanding the pH effects. At pH 5.5 deposition increases with an increase in temperature (Figures 5.18a and 5.18b), whereas at pH 7.0 deposition decreases with an increase in temperature (Figures 5.18c and 5.18d).

Temperature will have a greater effect on the physical properties of the components such as viscosity than on chemical properties. Nevertheless, temperature is known to affect solubility. The solubility of resin acids increases with increasing temperature [54]. As a result the temperature-dependent deposition can be partly explained in terms of solubility.

At pH 5.5, 20°C deposition is caused by an interaction between *FAP-RAP* where only a small amount of each component is soluble. At the same pH (i.e. 5.5) but a higher temperature (i.e. 50°C) the deposition is no longer as multi-component interaction based but primarily *RAP* driven. This is due to the fact that a higher percentage of the soluble material is *RAP* at this higher temperature, suggesting that the fatty acid solubility is still primarily determined by pH. Temperature driven *RAP* solubility is also supported by depositions at pH 7.0, 50°C where the contour lines are nearly horizontal, at moderate to high resin acid levels, suggesting that deposition is heavily driven by *RAP*. At low resin acid concentrations the *RAP-FAP* interaction

dominates. The impact of temperature on *RAP* solubility can also help to explain why there is more interaction between components (greater contour line curvature) at lower temperatures, as there are more similar concentrations of each component in solution (i.e. less resin acid in solution).

Although this soluble fraction-driven pitch deposition is a simplified view of what might actually be happening, it does help to explain the general changes in depositions observed at these pHs and temperatures using the three model components for *RAP*, *FAP* and *GLP*. There are obviously other factors also influencing pitch deposition. By conducting more experiments using these deposition and modelling techniques hopefully the nature of pitch deposition will eventually be more fully understood.

Back[54] said that for a good understanding of pitch problems it is a great advantage to combine the maximum number of tests (e.g. deposition, particle count, particle size, etc.). Depositions measurements and surface tension were taken of the solutions before and after deposition, during the pH 7.0, 50°C depositions, in order to gain insight into the understanding of the relationship of pitch deposition and surface tension. Nguyen[106] was able to show impact of surface tension on the prevention of pitch deposition, this work however did not show any impact of surface tension on deposition. Both Figures 3.36 and 3.37 show that the surface tension is lowest when the solutions are primarily fatty acid and that the surface tensions are highest when the solution composition is either primarily resin acid or primarily triglyceride. Surface tensions provide little insight, at this point, as they reflect the individual surface tensions of the fatty acid, resin acid and triglycerides. It would be interesting to further study how the low point of deposition at pH 7.0, 50°C is related to the low surface tensions measured at the same point prior to deposition.

Paper mills that wish to assess the potential pitch deposition based on the extractive content and composition of their wood pulp(s) can use these models. In the event that online measurement of extractives was to become available these models could be used to predict deposition and control fixative/dispersant strategies. A potential application of this is shown in Figure 5.23 where TPD is predicted using paper mill extractive data, from Norske Skog's Albury mill, and models developed in this thesis.

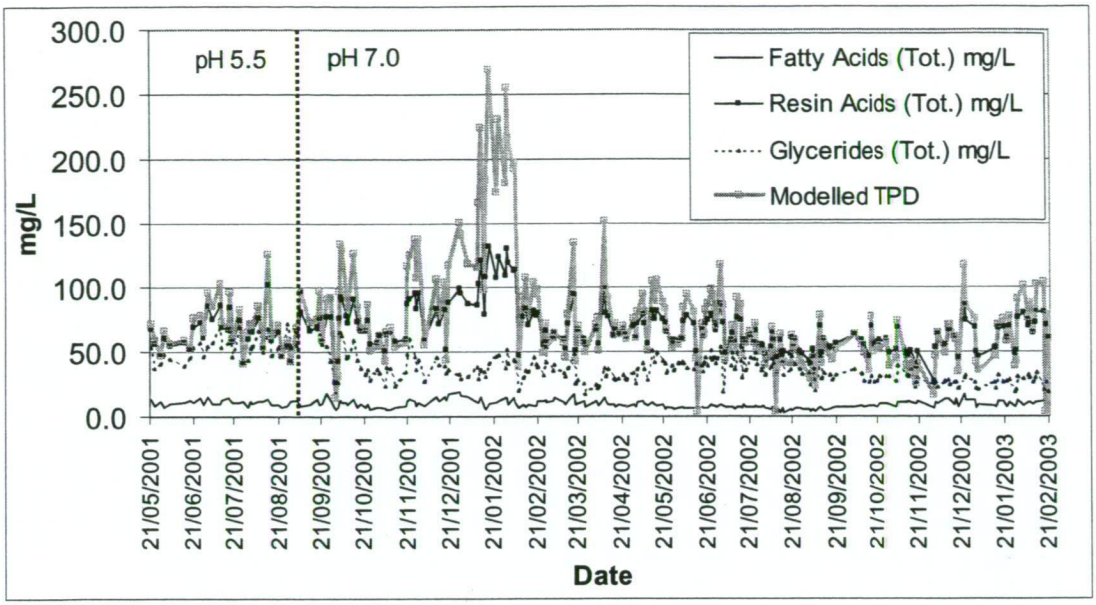


Figure 5.23. Summary of model surface plots for each of the pH and temperature conditions.

Figure 5.23 makes use of statistical deposition models developed in the results section for pH 7.0 and 5.5 at 50°C. The vertical dotted line on the figure indicates when this transition in pH occurred on the papermachine at Albury. The grey line indicates what the predicted *TPD* was for each of the measured extractive levels. *TPD* appears to follow *RAP* quite well, as predicted by the statistical deposition modelling, with the highest predicted deposition being when *GLP* and *RAP* are dissimilar. Focusing on reducing the variability in the *RAP* should be the focus of the Albury mill based on these model predictions. Although there is no mill data which can be directly correlated to this estimated deposition, the employees at the paper mill confirm that the point of high predicted deposition do concur with pitch deposition difficulties observed at the Norske Skog Albury site.

The ability to get a better understanding of how and what is happening in regards to pitch deposition, due to this work, has however helped Norske Skog Albury to understand why certain control strategies are more effect under different conditions of pH and temperature[25].

6. CONCLUSIONS

This is the summary of the conclusions arrived at in the previous chapters.

6.1 Experimental methods

The laboratory and analytical methods used and developed, throughout this thesis, allowed for reproducible and reliable measurement of extractive levels.

The statistical modelling and model visualisation techniques allowed for easy identification of component interactions and subsequent control strategy recommendations. This was achieved through thorough modelling techniques and the subsequent rigorous testing of the models developed.

6.2 Deposition behaviour

Deposition was dependent on composition quantities and interaction of components, pH and temperature. As a result deposition behaviour was different for all temperature and pH conditions evaluated.

pH 5.5 at 20°C

The interaction between resin and fatty acids are primarily responsible for depositions at these conditions of temperature and pH.

pH 7.0 at 20°C

Triglycerides and resin acids interact under these conditions, the result of which is pitch deposition.

pH 5.5 at 50°C

Deposition under these temperature and pH conditions is proportional to resin acid concentration.

pH 7.0 at 50°C

Resin and fatty acids as well as triglycerides interact and form pitch deposition at these modern papermaking condition. Although fatty acids play a role in this interaction it is the interaction between the resin acids and triglycerides that is the predominant cause of this deposition. Of the resin acid and triglyceride the resin acid levels are more responsible for pitch deposition.

6.3 Control strategies

The differences in deposition behaviours required differences in control strategies.

pH 5.5 at 50°C

Removal of resin acids and/or fixation of resin acids to the wood pulp fibres would be an effective means of controlling pitch depositions under these conditions of temperature and pH.

pH 7.0 at 50°C

Similar to conditions of 5.5 pH at 50°C removal and/or fixation of resin acids would be the most effective means at decreasing pitch deposition. However at pH 7.0 if the solution becomes primarily triglyceride in nature, through the removal of resin acids from the system, then deposition will begin to increase. As a result one needs to balance the fixation and/or removal of both the triglyceride and resin acid levels. One means of accomplishing this is through the hydrolysis of triglycerides to fatty acids in coordination with the seasonal variation of triglyceride levels.

6.4 Interaction mechanisms

There is evidence to suggest that previously proposed interaction mechanisms of viscosity, colloidal stability and solubility may help to support the theory that hydrogen bonding between the soluble molecules of the individual extractive components is responsible for pitch deposition.

Increasing the temperature decreases viscosity and increases the solubilities and

interaction of the extractive components; leading to the potential of increased deposition.

Increasing the pH increases the solubilities of the extractive components but increases the deprotonation of the carboxylic acid groups thus decreasing their ability to hydrogen bond with functional groups of other extractive compounds.

7. FUTURE WORK

No work is ever truly authoritative, or complete, and as such the author recommends that the following topics should be further investigated.

7.1 Experimental methods

Studies should include the measurement of pitch particle sizes as both Garver *et al*[48] and Swerin *et al*[11] found them to be important in understanding how different fixatives work.

Improved GC methods should include the exploration of shorter column length as described by Gutiérrez *et al*[152]. Their work showed that improvements in narrowing triglyceride peak widths could be achieved by reduced column length, though possibly at the expense of widening fatty and resin acid peak widths.

Methods should be developed such that wood fibre can be part of the deposition experiments. The important role of fibre, as a substrate for fixation and mechanical entrapment of extractives, has been highlighted as significant by others[16, 114, 164]. The addition of wood polysaccharides and simple electrolytes should also be explored as they appear to have an effect on colloidal stability[19, 62, 78, 126-129].

Statistical modelling of deposition data should be conducted to determine whether the deposition of specific components is closely related to their concentrations prior to do deposition, rather than focussing solely on total pitch deposited.

7.2 Deposition behaviour

The interaction between fatty acids, resin acids, triglycerides, sterols and steryl esters should be explored as others have found sterols and steryl esters to be an important contributor to pitch deposition[67, 119, 120, 124, 125].

A variety of pure triglycerides, resin and fatty acids of varying chemical structure should be evaluated in order to better understand functional group-specific deposition behaviour.

A more detailed range of deposition pHs and temperatures should be explored in order to better understand their influence on pitch deposition.

7.3 Control strategies

The investigation of the proposed control strategies should be conducted in order to prove or disprove the theories developed. Methods would need to be developed through inspiration of the works of others[16, 25, 55]. These methods should also be used to evaluated control strategies not proposed within this work (i.e.dispersants).

7.4 Interaction mechanisms

Vercoe[161] has gone some way in showing that interactions are occurring between extractive molecules through deposition work and computer molecular modelling. Further work needs to be done to prove of disprove whether or not this is occurring between soluble molecules or between micelles.

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APPENDIX A - pH PROBE

Maintenance of a pH probe in wood extractive solutions

The pH of the deposition solutions was measured using an ORION Triode™ pH electrode model: 91-57BN. Special care and use of the probe was required to ensure accurate and reproducible pH readings of the deposition solution. These procedures are based on the electrode maintenance procedures described in the pH probe manual[165].

Whilst not in use the pH probe was stored in a saturated potassium chloride (KCl, BDH 99.8% purity) solution, the pH probe reference chamber was also filled with the saturated KCl solution as well.

Two days before using the probe it was stored in a 0.1M hydrochloric acid (HCl) solution. The day before use day the pH probe was stored in a saturated KCl solution and the pH probe reference chamber was filled with Milli-Q® water. The morning that the pH probe was used the reference chamber was filled with fresh saturated KCl solution. This was a variation on electrode maintenance procedures described in the pH probe manual[165].

The pH was calibrated using pH 4, pH 7 and pH 10 buffer solutions from BDH. The temperature adjusted buffer concentrations were used to establish the pH measurement reference slope.

A series of "quick rinses", based on electrode maintenance procedures described in the pH probe manual[165], were also used in between measuring of deposition solutions. The first "quick rinse" was of a beaker containing laboratory grade methanol, this was in attempt to remove the fatty acids and triglycerides. The second "quick rinse" was of a beaker containing laboratory grade acetone, this was to try and further dissolve any extractives that had agglomerated on the pH probe. The third "quick rinse" was of beaker containing 0.1 M HCl, this was used as a general cleaning of the probe. The fourth and fifth "quick rinses" were beakers containing the standard dialysis wash solution comprised of distilled water, which had been brought to pH 5 using 0.16M HNO_3 and contained a slight electrolytic residual of

0.001M KNO_3. This rinsing method is depicted graphically in Figure A.1.

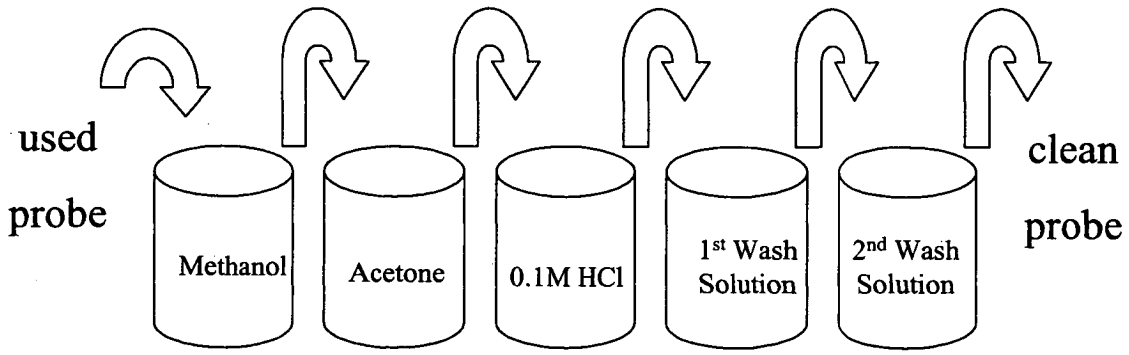


Figure A.1. Rinsing method for pH probe between measurements.

When pH measurement began to drift the probe was placed in the third "quick rinse" beaker (HCl) for 2-3 minutes and the deposition solution pH was tested using pH test strips (Sigma P-4411 pH 7.0-14.0 and P-4661 pH 0.0-6.0) to verify whether the pH probe had been reading properly.

APPENDIX B - VARIAN 3800 GC METHOD

```
Star Chromatography Workstation - Method Listing   Fri Mar 21 09:45:59 2003

Method  Boyer15m

********************************************************************************

**********************
    3800 GC
**********************
Module Address: 44

8400 Autosampler
----------------
                        Syringe Size  10 uL
                      Injection Mode  Std On Column
          Solvent Penetration Depth  90 %
           Sample Penetration Depth  90 %

                 Default Clean Vial  I
              Default Clean Volume  5.0 uL
             Default Clean Strokes  1
          Default Clean Drawup Speed  5.0 uL/sec

 Clean Mode Pre-Inj Solvent Flushes  3
Clean Mode Post-Inj Solvent Flushes  1
  Clean Mode Pre-Inj Sample Flushes  0
           Clean Mode Solvent Source  I

Valve Table
-----------

 Front Injector Type 1079
-------------------------
            Oven Power: On
               Coolant: On
     Enable Coolant at: 167 C
       Coolant Timeout: 20.00 min

     Temp     Rate      Hold      Total
      (C)   (C/min)    (min)      (min)
     --------------------------------
       90        0      0.50       0.50
      325      200     20.00      21.68

      Time    Split    Split
      (min)   State    Ratio
      -----  -------  ------
    Initial    Off       Off

 Front Injector EFC Type 1
-------------------------
 Pressure     Rate      Hold      Total
    (psi) (psi/min)    (min)      (min)
 -------------------------
      3.0     0.00     32.67      32.67

Column Oven
-----------
              Coolant  Off
     Enable Coolant at  50 C
       Coolant Timeout  20.00 min
    Stabilization Time  2.00 min

     Temp     Rate      Hold      Total
      (C)   (C/min)    (min)      (min)
     ----------------------
       90      0.0      1.50       1.50
      320     12.0     12.00      32.67

 Front FID Detector
-------------------
      Oven Power: On
     Temperature: 360 C
     Electronics: On
   Time Constant: Fast
```

	Time (min)	Range	Autozero
Initial		11	yes

Output Port A

	Time (min)	Signal Source	Attenuation
Initial		Front	1

Output Port B

	Time (min)	Signal Source	Attenuation
Initial		Front	1

Output Port C

	Time (min)	Signal Source	Attenuation
Initial		Front	1

Data Acquisition

```
      Detector Bunch Rate : 4 points (10.0 Hz)
           Monitor Length : 64 bunched points (6.4 sec)
       Front FID/TSD Scale: 10 Volts
      Middle FID/TSD Scale: 1 Volts
        Rear FID/TSD Scale: 1 Volts
```

Integration Parameters Address 44 Channel Front

```
Subtract Blank Baseline      : No
Initial S/N Ratio            : 3
Initial Peak Width           : 2 sec
Initial Tangent Height %     : 0%
Monitor Noise                : Before every run
Measurement Type             : Peak Area
Initial Peak Reject Value    : 1500    counts
Report Unidentified Peaks    : Yes
Report Missing Peaks         : Yes
Normalize Results            : No
```

Calibration Setup Address 44 Channel Front

```
Calculation Type             : Internal Standard
Number of Calibration Levels: 10
Curve Origin                 : Force
Curve Fit                    : Linear
Weighted Regression          : (None)
Replicate Treatment          : Keep Replicates Separate
Replicate Tolerance          : Add replicates within tolerance of  10.0%
   Out-of-Tolerance Action   : No Action
Calibration Range Tolerance  :      10.0%
    Out-of-Tolerance Action  : No Action
```

Verification Setup Address 44 Channel Front

```
Deviation Tolerance          : 100.0%
    Out-of-Tolerance Action  : No Action
```

Peak Table Address 44 Channel Front

```
Reference Peaks Time Windows:Width:  0.10 min.  Retention Time 2.0%
Other Peaks Time Windows    :Width:  0.10 min.  Retention Time 2.0%

Peak Name       : C15:0
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:0  Time:   6.160 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +1.0060e+000x +0.0000e+000

Peak Name       : C17:0 INT STD
Attributes      : Ref:Y  Std:Y  RRT:Y  Lock:Y  Group:0  Time:   7.681 min
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +1.0000e+000x +0.0000e+000

Peak Name       : C18x
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:1  Time:   8.100 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +9.9700e-001x +0.0000e+000

Peak Name       : pimaric
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   8.380 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : sandaracopimaric
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   8.490 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000
```

```
Peak Name       : isopimaric
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   8.585 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : palustric
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   8.740 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : dehydroabiet
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   8.960 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : abietic acid
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:   9.060 min
Uses Standard   : C17:0 INT STD
Level  1 Amount  1
Level  2 Amount  1
Level  3 Amount  1
Level  4 Amount  1
Level  5 Amount  1
Level  6 Amount  1
Level  7 Amount  1
Level  8 Amount  1
Level  9 Amount  1
Level 10 Amount  1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : neoabietic
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:2  Time:  10.020 min
Uses Standard   : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients    : +0.0000e+000x^3 +0.0000e+000x^2 +8.4900e-001x +0.0000e+000

Peak Name       : Chol. Stear.
Attributes      : Ref:N  Std:N  RRT:N  Lock:Y  Group:0  Time:  20.900 min
```

```
Uses Standard  : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients   : +0.0000e+000x^3 +0.0000e+000x^2 +8.0800e-001x +0.0000e+000

Peak Name        D.O.G.
Attributes       Ref:N  Std:N  RRT:N  Lock:Y  Group:0  Time:  23.000 min
Uses Standard    C17:0 INT STD
Level  1 Amount  1
Level  2 Amount  1
Level  3 Amount  1
Level  4 Amount  1
Level  5 Amount  1
Level  6 Amount  1
Level  7 Amount  1
Level  8 Amount  1
Level  9 Amount  1
Level 10 Amount  1
Coefficients     +0.0000e+000x^3 +0.0000e+000x^2 +6.7000e-001x +0.0000e+000

Peak Name      : triolene
Attributes     : Ref:N  Std:N  RRT:N  Lock:Y  Group:3  Time:  25.700 min
Uses Standard  : C17:0 INT STD
Level  1 Amount: 1
Level  2 Amount: 1
Level  3 Amount: 1
Level  4 Amount: 1
Level  5 Amount: 1
Level  6 Amount: 1
Level  7 Amount: 1
Level  8 Amount: 1
Level  9 Amount: 1
Level 10 Amount: 1
Coefficients   : +0.0000e+000x^3 +0.0000e+000x^2 +5.0400e-001x +0.0000e+000


Time Events Table   Address 44  Channel Front
-----------------------------------------
Width Event         :     0.0000  4.0   sec
Inhibit Integrate   :     0.0100  until      4.5000
Solvent Reject      :     9.3500  until     12.0000
Inhibit Integrate   :    12.0000  until     20.3000
Width Event         :    22.0000  8.0   sec
Inhibit Integrate   :    30.0000  until     32.6700
```

APPENDIX C - pH 5.5, 50°C DATA

Table C.1. Deposition data for pH 5.5, 50°C.

	Jar	FAP	RAP	GLP	B1	B2	B3	B4	B5	B8	TPD	Model	Residual
11-Dec-01	B	33.915	57.665	23.7	12.31115	40.82682	2.607	-19.55708	-6.430284	19.95151	51.79563	50.22803	1.567593
11-Dec-01	D	33.405	86.24	21.13	12.12602	61.05792	2.3243	-28.80847	-5.646781	44.62403	111.4104	87.09841	24.312
11-Dec-01	I	29.06	33.19	33.35	10.54878	23.49852	3.6685	-9.645014	-7.753208	6.609457	31.58	27.16109	4.418914
11-Dec-01	J	24.06	77.915	25.53	8.73378	55.16382	2.8083	-18.74635	-4.914014	36.42448	90.04	80.81757	9.22243
11-Dec-01	L	46.945	62.49	28.54	17.04104	44.24292	3.1394	-29.33593	-10.71848	23.43	52.635	48.26835	4.366648
11-Dec-01	N	37.625	46.595	17.96	13.65788	32.98926	1.9756	-17.53137	-5.40596	13.02656	19.245	38.91705	-19.67205
1-Oct-01	B	5.275	20.575	8.025	1.914825	14.5671	0.88275	-1.085331	-0.338655	2.539984	22.795	18.59022	4.20478
1-Oct-01	C	4.77	25.64	6.26	1.73151	18.15312	0.6886	-1.223028	-0.238882	3.944458	28.405	23.23024	5.174763
1-Oct-01	D	3.76	34.25	4.15	1.36488	24.249	0.4565	-1.2878	-0.124832	7.038375	34.21	32.02472	2.185283
1-Oct-01	E	3.675	56.755	5.065	1.334025	40.18254	0.55715	-2.085746	-0.148911	19.32678	53.415	60.09827	-6.683268
1-Oct-01	F	5.765	12.045	9.38	2.092695	8.52786	1.0318	-0.694394	-0.432606	0.870492	14.215	11.43452	2.780481
1-Oct-01	G	17.1	11.605	10.395	6.2073	8.21634	1.14345	-1.984455	-1.422036	0.808056	17.14	12.98587	4.154127
1-Oct-01	H	33.95	12.36	10.225	12.32385	8.75088	1.12475	-4.19622	-2.77711	0.916618	19.965	16.12439	3.840615
1-Oct-01	I	36.245	11.51	10.365	13.15694	8.14908	1.14015	-4.1718	-3.005435	0.794881	9.175	16.04641	-6.871405
1-Oct-01	J	39.795	10.785	9.085	14.44559	7.63578	0.99935	-4.291891	-2.892301	0.697897	10.635	16.56354	-5.928544
22-Oct-01	A	17.836	33.736	19.147	6.474468	23.88509	2.10617	-6.017153	-2.732047	6.828706	36.494	30.77123	5.722765
22-Oct-01	B	15.79	32.255	44.285	5.73177	22.83654	4.87135	-5.093065	-5.594081	6.24231	24.14	29.31488	-5.174884
22-Oct-01	F	16.095	17.59	51.41	5.842485	12.45372	5.6551	-2.831111	-6.619552	1.856449	14.015	16.5629	-2.547898
22-Oct-01	G	14.32	30.04	35.225	5.19816	21.26832	3.87475	-4.301728	-4.035376	5.41441	22.26	27.67627	-5.416273
22-Oct-01	H	14.325	40.045	40.28	5.199975	28.35186	4.4308	-5.736446	-4.616088	9.621612	30.64	37.69311	-7.053113
22-Oct-01	K	5.805	22.079	36.079	2.107215	15.63193	3.96869	-1.281686	-1.675509	2.924893	12.993	21.84453	-8.851528
22-Oct-01	L	15.12	23.975	38.015	5.48856	16.9743	4.18165	-3.62502	-4.598294	3.448804	13.055	22.06743	-9.012427
22-Oct-01	M	27.54	26.115	41.575	9.99702	18.48942	4.57325	-7.192071	-9.159804	4.091959	11.735	21.03595	-9.300948
22-Oct-01	N	38.79	28.55	33.455	14.08077	20.2134	3.68005	-11.07455	-10.38176	4.890615	11.855	21.57865	-9.723655
22-Oct-01	Q	54.85	31.685	40.215	19.91055	22.43298	4.42365	-17.37922	-17.64634	6.023635	18.09	17.98038	0.109619
29-Oct-01	A	16.488	15.967	23.904	5.985144	11.30464	2.62944	-2.632639	-3.153033	1.529671	22.269	15.7498	6.519196
29-Oct-01	B	13.77	26.39	18.29	4.99851	18.68412	2.0119	-3.633903	-2.014826	4.178593	23.545	24.37841	-0.833407
29-Oct-01	C	13.385	32.515	19.965	4.858755	23.02062	2.19615	-4.352133	-2.137852	6.343351	38.095	30.17315	7.921851
29-Oct-01	D	12.76	60.08	18.46	4.63188	42.53664	2.0306	-7.666208	-1.884397	21.65764	63.6	62.20965	1.390355
29-Oct-01	E	10.825	88.415	20.23	3.929475	62.59782	2.2253	-9.570924	-1.751918	46.90327	97.435	106.4547	-9.019676
29-Oct-01	F	7.06	14.74	44.66	2.56278	10.43592	4.9126	-1.040644	-2.522397	1.303606	23.975	15.77146	8.203542
29-Oct-01	G	5.32	24.38	33.425	1.93116	17.26104	3.67675	-1.297016	-1.422568	3.566306	24.63	23.90946	0.720535
29-Oct-01	H	5.225	35.535	43.995	1.896675	25.15878	4.83945	-1.856704	-1.838991	7.576417	40.635	36.17185	4.463151
29-Oct-01	I	4.835	69.02	39.64	1.755105	48.86616	4.3604	-3.337117	-1.533275	28.58256	88.865	80.10427	8.760733
29-Oct-01	K	6.217	11.557	62.813	2.256771	8.182356	6.90943	-0.718499	-3.124067	0.801385	18.067	14.43424	3.632758
29-Oct-01	L	6.025	24.15	82.11	2.187075	17.0982	9.0321	-1.455038	-3.957702	3.499335	31.945	26.6755	5.269503
29-Oct-01	M	5.425	35.88	73.815	1.969275	25.40304	8.11965	-1.94649	-3.203571	7.724246	51.43	38.51447	12.91553
30-Oct-02	F	14.15	12.68	0	5.13645	8.97744	0	-1.79422	0	0.964694	19.73	13.27251	6.457492
30-Oct-02	G	15.38	21.4	0	5.58294	15.1512	0	-3.29132	0	2.74776	26.405	20.21832	6.186679
30-Oct-02	H	11.045	30.225	0	4.009335	21.3993	0	-3.338351	0	5.481304	36.99	27.72007	9.269934
30-Oct-02	I	13.425	33.59	0	4.873275	23.78172	0	-4.509458	0	6.769729	41.205	31.10779	10.09721
30-Oct-02	M	2.285	15.58	12.38	0.829455	11.03064	1.3618	-0.356003	-0.226306	1.456418	17.08	14.17301	2.906994
30-Oct-02	N	0.65	20.52	12.095	0.23595	14.52816	1.33045	-0.13338	-0.062894	2.526422	23.975	18.56126	5.413737
5-Dec-01	A	16.591	53.074	53.467	6.022533	37.57639	5.88137	-8.805507	-7.096568	16.9011	66.127	51.25993	14.86707
5-Dec-01	C	41.485	50.775	48.925	15.05906	35.9487	5.38175	-21.06401	-16.23723	15.4686	33.665	35.08632	-1.421318
5-Dec-01	D	17.06	61.15	54.33	6.19278	43.2942	5.9763	-10.43219	-7.414958	22.43594	63.17	61.067	2.103005
5-Dec-01	E	33.55	56.83	50.005	12.17865	40.23564	5.50055	-19.06647	-13.42134	19.37789	32.525	45.52508	-13.00008
5-Dec-01	F	12.735	35.1	64.88	4.622805	24.8508	7.1368	-4.469985	-6.609974	7.39206	25.675	33.35992	-7.684925
5-Dec-01	G	25.09	41.315	31.63	9.10767	29.25102	3.4793	-10.36593	-6.348774	10.24158	29.45	35.71855	-6.26855
5-Dec-01	I	50.29	43.75	42.49	18.25527	30.975	4.6739	-22.00188	-17.09458	11.48438	10.19	26.60587	-16.41587
5-Dec-01	J	29.3	42.44	76.16	10.6359	30.04752	8.3776	-12.43492	-17.8519	10.80692	24.88	30.23911	-5.359113
5-Dec-01	K	25.576	39.662	53.753	9.284088	28.0807	5.91283	-10.14395	-10.99829	9.438445	23.296	32.03685	-8.740854
5-Dec-01	L	38.7	44.475	84.085	14.0481	31.4883	9.24935	-17.21183	-26.03272	11.86815	27.445	24.19144	3.253562
5-Dec-01	N	48.62	43.51	54.725	17.64906	30.80508	6.01975	-21.15456	-21.28584	11.35872	21.56	23.85706	-2.297064
5-Nov-02	A	0	35.035	9.63	0	24.80478	1.0593	0	0	7.364707	35.035	33.61888	1.416122
5-Nov-02	B	0	12.265	49.2	0	8.68362	5.412	0	0	0.902581	17.165	15.06139	2.103607
5-Nov-02	C	0	22.855	39.455	0	16.18134	4.34005	0	0	3.134106	21.235	23.8337	-2.598698
5-Nov-02	D	0	37.995	49	0	26.90046	5.39	0	0	8.66172	53.095	41.41908	11.67592
5-Nov-02	E	0	36.645	27.395	0	25.94466	3.01345	0	0	8.057136	51.07	37.44554	13.62446
5-Nov-02	F	22.535	0	28.155	8.180205	0	3.09705	0	-5.075783	0	7.21	6.356718	0.853282
5-Nov-02	G	27.345	0	47.165	9.926235	0	5.18815	0	-10.31782	0	0.805	5.110888	-4.305888
5-Nov-02	H	34.165	0	1.4	12.4019	0	0.154	0	-0.382648	0	4.765	12.18254	-7.417541
5-Nov-02	I	18.73	0	29.96	6.79899	0	3.2956	0	-4.489206	0	8.94	5.744041	3.195959
5-Nov-02	J	17.8	0	61.655	6.4614	0	6.78205	0	-8.779672	0	3.745	4.737015	-0.992015
5-Nov-02	K	15.925	0	17.04	5.780775	0	1.8744	0	-2.170896	0	9.135	5.5515	3.5835
5-Nov-02	L	0	10.31	30.955	0	7.29948	3.40505	0	0	0.637777	11.53	11.38669	0.14331
5-Nov-02	M	0	11.435	63.285	0	8.09598	6.96135	0	0	0.784555	13.02	15.90229	-2.882287
5-Nov-02	N	35.965	10.88	1.345	13.0553	7.70304	0.14795	-3.912992	-0.386983	0.710246	30.62	17.2245	13.3955
5-Nov-02	Q	0	0	26.2	0	0	2.882	0	0	0	-1.32	2.888575	-4.208575
6-Nov-01	A	5.768	17.483	66.769	2.093784	12.37796	7.34459	-1.008419	-3.080989	1.833932	18.51	19.73175	-1.221746
6-Nov-01	B	11.56	15.16	40.55	4.19628	10.73328	4.4605	-1.752496	-3.750064	1.378954	14.675	15.3991	-0.724104
6-Nov-01	C	21.835	15.42	50.01	7.926105	10.91736	5.5011	-3.366957	-8.735747	1.426658	19.53	13.8939	5.636099
6-Nov-01	D	36.275	16.195	65.37	13.16783	11.46606	7.1907	-5.874736	-18.97037	1.573668	25.83	9.000143	16.82986
6-Nov-01	E	53.905	15.405	57.31	19.56752	10.90674	6.3041	-8.304065	-24.71436	1.423884	22.485	5.701023	16.78398

Table C.2. Test deposition data for pH 5.5, 50°C.

	Jar	Sample	FAP	RAP	GLP	TPD
1-Oct-01	A	16	5.2	9.9	8.0	11.2
22-Oct-01	I	34	13.0	58.5	41.5	78.1
6-Nov-01	Q	110	44.9	35.2	16.4	19.9
5-Dec-01	B	67	31.3	63.5	55.5	52.3

11-Dec-01	A	1	19.2	12.9	19.4	7.6

Modelling data for depositions at pH 5.5, 50°C

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\pH5.5stats\55.SYD, created Tue Feb 18, 2003 at 19:44:02, contains variables:

FAP RAP GLP TPD

111 cases and 4 variables processed and saved.

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\pH5.5stats\55respfact.SYD, created Tue Feb 18, 2003 at 19:46:11, contains variables:

FAP RAP GLP TPD

Dep Var: TPD N: 111 Multiple R: 0.924 Squared multiple R: 0.853

Adjusted squared multiple R: 0.840 Standard error of estimate: 8.440

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	5.617	3.298	0.000	.	1.703	0.092
FAP	0.224	0.191	0.159	0.079	1.174	0.243
RAP	0.477	0.144	0.459	0.076	3.314	0.001
GLP	0.053	0.120	0.063	0.071	0.443	0.659
FAP*FAP	0.001	0.004	0.017	0.088	0.135	0.893
RAP*FAP	-0.010	0.003	-0.292	0.181	-3.263	0.002
GLP*FAP	-0.006	0.002	-0.233	0.212	-2.819	0.006
RAP*RAP	0.008	0.002	0.568	0.112	4.972	0.000
GLP*RAP	0.003	0.002	0.144	0.193	1.656	0.101
GLP*GLP	-0.001	0.001	-0.059	0.084	-0.447	0.656

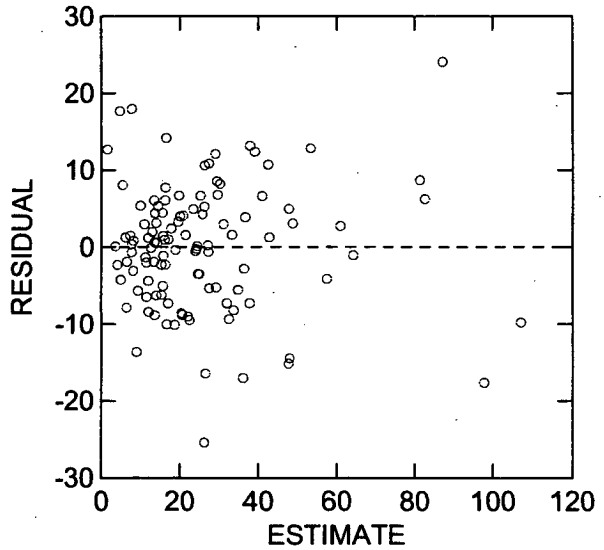
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	41767.696	9	4640.855	65.157	0.000
Residual	7193.832	101	71.226		

*** WARNING ***
Case 2 has large leverage (Leverage = 0.326)
Case 2 is an outlier (Studentized Residual = 3.685)
Case 30 has large leverage (Leverage = 0.298)
Case 53 has large leverage (Leverage = 0.291)
Case 79 has large leverage (Leverage = 0.260)
Case 89 has large leverage (Leverage = 0.304)
Case 96 has large leverage (Leverage = 0.281)
Case 103 has large leverage (Leverage = 0.306)

Durbin-Watson D Statistic 1.366
First Order Autocorrelation 0.313

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 111 Multiple R: 0.921 Squared multiple R: 0.849

Adjusted squared multiple R: 0.837 Standard error of estimate: 8.518

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.421	0.154	0.453	0.054	2.739	0.007
RAP	0.652	0.101	1.009	0.061	6.457	0.000
GLP	0.151	0.106	0.279	0.039	1.426	0.157
FAP*FAP	-0.001	0.004	-0.050	0.063	-0.324	0.747
RAP*FAP	-0.011	0.003	-0.424	0.134	-4.038	0.000
GLP*FAP	-0.008	0.002	-0.344	0.161	-3.583	0.001
RAP*RAP	0.007	0.001	0.582	0.095	4.667	0.000
GLP*RAP	0.002	0.002	0.107	0.133	1.010	0.315
GLP*GLP	-0.001	0.001	-0.123	0.053	-0.739	0.461

Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	41561.146	8	5195.143	71.605	0.000
Residual	7400.382	102	72.553		

*** WARNING ***

Case 2 has large leverage (Leverage = 0.317)

Case 2 is an outlier (Studentized Residual = 3.854)

Case 30 has large leverage (Leverage = 0.298)

Case 53 has large leverage (Leverage = 0.257)

Case 74 has large leverage (Leverage = 0.255)

Case 79 has large leverage (Leverage = 0.260)

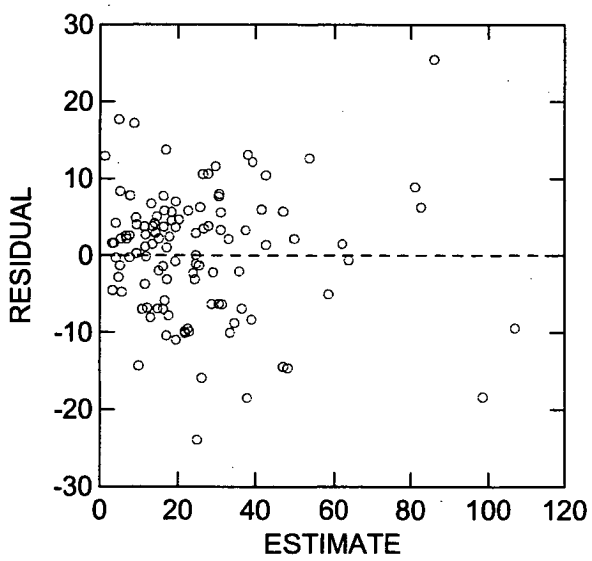
Case 89 has large leverage (Leverage = 0.304)

Case 96 has large leverage (Leverage = 0.281)

Case 103 has large leverage (Leverage = 0.303)

Durbin-Watson D Statistic 1.390
First Order Autocorrelation 0.302

Plot of Residuals against Predicted Values



Step # 0 R = 0.924 R-Square = 0.853

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.224	0.191	0.159	0.07884	1	1.378	0.243
3	RAP	0.477	0.144	0.459	0.07574	1	10.983	0.001
4	GLP	0.053	0.120	0.063	0.07128	1	0.196	0.659
5	FAP*FAP	0.001	0.004	0.017	0.08836	1	0.018	0.893
6	RAP*FAP	-0.010	0.003	-0.292	0.18132	1	10.648	0.002
7	GLP*FAP	-0.006	0.002	-0.233	0.21235	1	7.949	0.006
8	RAP*RAP	0.008	0.002	0.568	0.11165	1	24.721	0.000
9	GLP*RAP	0.003	0.002	0.144	0.19301	1	2.741	0.101
10	GLP*GLP	-0.001	0.001	-0.059	0.08405	1	0.200	0.656
Out		Part. Corr.						
	none							

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.924 R-Square = 0.853
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.245	0.110	0.174	0.23711	1	5.010	0.027
3	RAP	0.478	0.143	0.461	0.07619	1	11.224	0.001
4	GLP	0.052	0.119	0.062	0.07160	1	0.191	0.663
6	RAP*FAP	-0.010	0.003	-0.291	0.18308	1	10.768	0.001
7	GLP*FAP	-0.006	0.002	-0.232	0.21821	1	8.118	0.005
8	RAP*RAP	0.008	0.002	0.566	0.11259	1	25.045	0.000
9	GLP*RAP	0.003	0.002	0.142	0.19813	1	2.767	0.099
10	GLP*GLP	-0.001	0.001	-0.057	0.08452	1	0.194	0.661
Out		Part. Corr.						
5	FAP*FAP	0.013	.	.	0.08836	1	0.018	0.893

Step # 2 R = 0.923 R-Square = 0.853
Term removed: GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.234	0.106	0.166	0.25103	1	4.866	0.030
3	RAP	0.470	0.141	0.453	0.07738	1	11.121	0.001
6	RAP*FAP	-0.009	0.003	-0.286	0.18681	1	10.661	0.001
7	GLP*FAP	-0.006	0.002	-0.225	0.22581	1	7.998	0.006
8	RAP*RAP	0.008	0.002	0.566	0.11259	1	25.275	0.000
9	GLP*RAP	0.004	0.002	0.154	0.22139	1	3.669	0.058
10	GLP*GLP	-0.000	0.001	-0.009	0.30441	1	0.017	0.896
Out		Part. Corr.						
4	GLP	0.043	.	.	0.07160	1	0.191	0.663
5	FAP*FAP	0.011	.	.	0.08875	1	0.011	0.916

Step # 3 R = 0.923 R-Square = 0.853
Term removed: GLP*GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.239	0.099	0.170	0.28576	1	5.827	0.018
3	RAP	0.477	0.130	0.460	0.09077	1	13.571	0.000
6	RAP*FAP	-0.009	0.003	-0.284	0.18999	1	10.833	0.001
7	GLP*FAP	-0.006	0.002	-0.231	0.32344	1	12.162	0.001
8	RAP*RAP	0.008	0.002	0.563	0.11750	1	26.345	0.000
9	GLP*RAP	0.004	0.002	0.148	0.33715	1	5.198	0.025
Out		Part. Corr.						
4	GLP	0.012	.	.	0.25786	1	0.014	0.905

5	FAP*FAP	0.010	.	.	0.08886	1	0.010	0.919
10	GLP*GLP	-0.013	.	.	0.30441	1	0.017	0.896

Dep Var: TPD N: 111 Multiple R: 0.923 Squared multiple R: 0.853

Adjusted squared multiple R: 0.844 Standard error of estimate: 8.326

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	6.024	2.257	0.000	.	2.669	0.009
FAP	0.239	0.099	0.170	0.286	2.414	0.018
RAP	0.477	0.130	0.460	0.091	3.684	0.000
RAP*FAP	-0.009	0.003	-0.284	0.190	-3.291	0.001
GLP*FAP	-0.006	0.002	-0.231	0.323	-3.487	0.001
RAP*RAP	0.008	0.002	0.563	0.117	5.133	0.000
GLP*RAP	0.004	0.002	0.148	0.337	2.280	0.025

Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	41751.733	6	6958.622	100.377	0.000
Residual	7209.794	104	69.325		

*** WARNING ***

Case 2 has large leverage (Leverage = 0.318)

Case 2 is an outlier (Studentized Residual = 3.681)

Case 30 has large leverage (Leverage = 0.294)

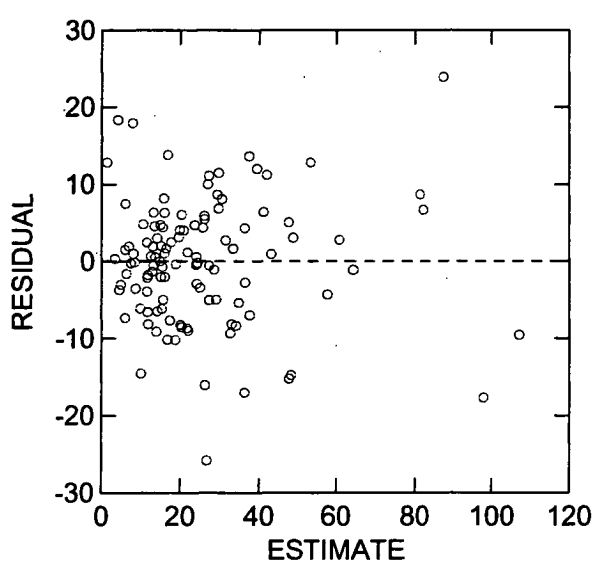
Case 79 has large leverage (Leverage = 0.238)

Case 103 has large leverage (Leverage = 0.297)

Durbin-Watson D Statistic 1.352

First Order Autocorrelation 0.320

Plot of Residuals against Predicted Values



Step # 0 R = 0.969 R-Square = 0.939

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.421	0.154	0.289	0.05412	1	7.502	0.007
2	RAP	0.652	0.101	0.643	0.06066	1	41.695	0.000
3	GLP	0.151	0.106	0.178	0.03860	1	2.034	0.157
4	FAP*FAP	-0.001	0.004	-0.032	0.06326	1	0.105	0.747
5	RAP*FAP	-0.011	0.003	-0.270	0.13431	1	16.305	0.000
6	GLP*FAP	-0.008	0.002	-0.219	0.16078	1	12.837	0.001
7	RAP*RAP	0.007	0.001	0.371	0.09516	1	21.777	0.000
8	GLP*RAP	0.002	0.002	0.068	0.13291	1	1.020	0.315
9	GLP*GLP	-0.001	0.001	-0.079	0.05330	1	0.546	0.461
Out		Part. Corr.						
	none							

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.969 R-Square = 0.938
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.378	0.079	0.260	0.20159	1	22.781	0.000
2	RAP	0.658	0.099	0.649	0.06245	1	44.034	0.000
3	GLP	0.159	0.103	0.187	0.04073	1	2.397	0.125
5	RAP*FAP	-0.012	0.003	-0.275	0.14026	1	17.748	0.000
6	GLP*FAP	-0.008	0.002	-0.225	0.17447	1	14.771	0.000
7	RAP*RAP	0.007	0.001	0.370	0.09526	1	21.892	0.000
8	GLP*RAP	0.002	0.002	0.069	0.13329	1	1.068	0.304
9	GLP*GLP	-0.001	0.001	-0.083	0.05416	1	0.623	0.432
Out		Part. Corr.						
4	FAP*FAP	-0.032	.	.	0.06326	1	0.105	0.747

Step # 2 R = 0.969 R-Square = 0.938
Term removed: GLP*GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.389	0.078	0.267	0.20722	1	24.802	0.000
2	RAP	0.686	0.093	0.676	0.07133	1	54.809	0.000
3	GLP	0.087	0.046	0.102	0.19937	1	3.498	0.064
5	RAP*FAP	-0.011	0.003	-0.268	0.14248	1	17.258	0.000
6	GLP*FAP	-0.008	0.002	-0.236	0.18438	1	17.195	0.000
	RAP*RAP							

7		0.006	0.001	0.357	0.09989	1	21.397	0.000
8	GLP*RAP	0.002	0.002	0.063	0.13488	1	0.912	0.342
Out		Part. Corr.						
4	FAP*FAP	-0.041	.	.	0.06427	1	0.177	0.675
9	GLP*GLP	-0.078	.	.	0.05416	1	0.623	0.432

Step # 3 R = 0.968 R-Square = 0.938
Term removed: GLP*RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.363	0.073	0.249	0.23547	1	24.585	0.000
2	RAP	0.708	0.089	0.699	0.07644	1	62.769	0.000
3	GLP	0.110	0.039	0.130	0.27917	1	7.944	0.006
5	RAP*FAP	-0.010	0.003	-0.247	0.16238	1	16.644	0.000
6	GLP*FAP	-0.008	0.002	-0.224	0.19345	1	16.301	0.000
7	RAP*RAP	0.006	0.001	0.357	0.09990	1	21.374	0.000
Out		Part. Corr.						
4	FAP*FAP	-0.045	.	.	0.06437	1	0.210	0.648
8	GLP*RAP	0.093	.	.	0.13488	1	0.912	0.342
9	GLP*GLP	-0.067	.	.	0.05480	1	0.464	0.497

Model contains no constant

Dep Var: TPD N: 111 Multiple R: 0.968 Squared multiple R: 0.938

Adjusted squared multiple R: 0.935 Standard error of estimate: 8.462

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.363	0.073	0.249	0.235	4.958	0.000
RAP	0.708	0.089	0.699	0.076	7.923	0.000
GLP	0.110	0.039	0.130	0.279	2.818	0.006
RAP*FAP	-0.010	0.003	-0.247	0.162	-4.080	0.000
GLP*FAP	-0.008	0.002	-0.224	0.193	-4.037	0.000
RAP*RAP	0.006	0.001	0.357	0.100	4.623	0.000

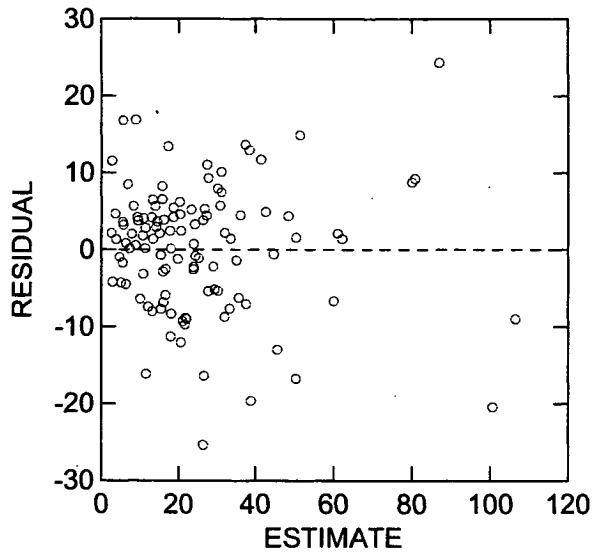
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	112932.399	6	18822.067	262.873	0.000
Residual	7518.144	105	71.601		

*** WARNING ***
Case 2 has large leverage (Leverage = 0.288)
Case 2 is an outlier (Studentized Residual = 3.593)
Case 30 has large leverage (Leverage = 0.293)
Case 79 has large leverage (Leverage = 0.224)
Case 103 has large leverage (Leverage = 0.263)

Durbin-Watson D Statistic 1.439
First Order Autocorrelation 0.276

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 111 Multiple R: 0.921 Squared multiple R: 0.848

Adjusted squared multiple R: 0.839 Standard error of estimate: 8.465

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.389	0.078	0.419	0.207	4.980	0.000
RAP	0.686	0.093	1.060	0.071	7.403	0.000
GLP	0.087	0.046	0.160	0.199	1.870	0.064
RAP*FAP	-0.011	0.003	-0.421	0.142	-4.154	0.000
GLP*FAP	-0.008	0.002	-0.369	0.184	-4.147	0.000
RAP*RAP	0.006	0.001	0.560	0.100	4.626	0.000
GLP*RAP	0.002	0.002	0.099	0.135	0.955	0.342

Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	41508.713	6	6918.119	96.539	0.000
Residual	7452.815	104	71.662		

*** WARNING ***

Case 2 has large leverage (Leverage = 0.310)

Case 2 is an outlier (Studentized Residual = 3.866)

Case 30 has large leverage (Leverage = 0.294)

Case 79 has large leverage (Leverage = 0.238)

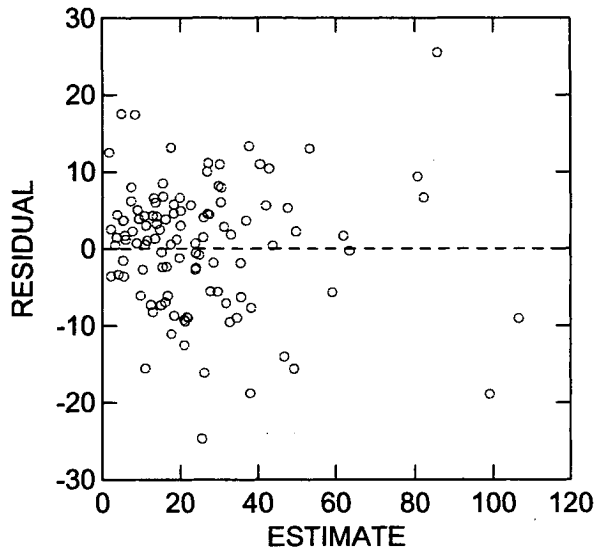
Case 89 has large leverage (Leverage = 0.214)

Case 103 has large leverage (Leverage = 0.298)

Durbin-Watson D Statistic 1.398

First Order Autocorrelation 0.297

Plot of Residuals against Predicted Values



Dep Var: TPD N: 111 Multiple R: 0.923 Squared multiple R: 0.853

Adjusted squared multiple R: 0.843 Standard error of estimate: 8.366

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	5.773	3.092	0.000	.	1.867	0.065
FAP	0.244	0.109	0.174	0.237	2.238	0.027
RAP	0.484	0.141	0.466	0.077	3.421	0.001
GLP	0.007	0.062	0.009	0.258	0.120	0.905
RAP*FAP	-0.009	0.003	-0.284	0.190	-3.270	0.001
GLP*FAP	-0.006	0.002	-0.236	0.222	-2.942	0.004
RAP*RAP	0.008	0.002	0.561	0.114	5.005	0.000
GLP*RAP	0.003	0.002	0.141	0.198	1.663	0.099

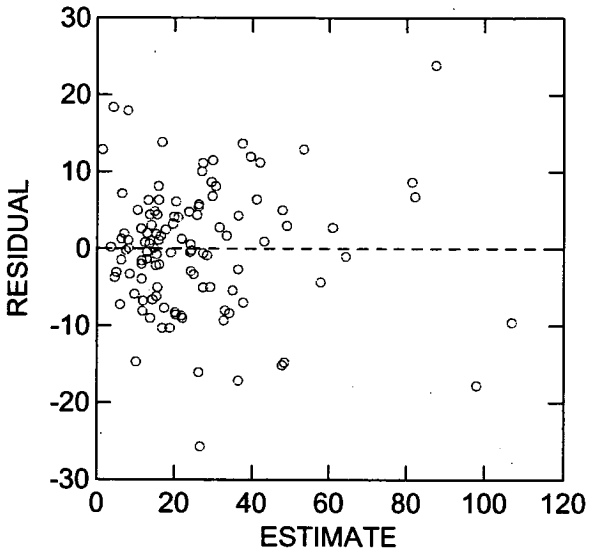
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	41752.735	7	5964.676	85.224	0.000
Residual	7208.792	103	69.988		

*** WARNING ***
Case 2 has large leverage (Leverage = 0.322)
Case 2 is an outlier (Studentized Residual = 3.664)
Case 30 has large leverage (Leverage = 0.295)
Case 79 has large leverage (Leverage = 0.239)
Case 103 has large leverage (Leverage = 0.303)

Durbin-Watson D Statistic 1.356
First Order Autocorrelation 0.318

Plot of Residuals against Predicted Values



APPENDIX D - pH 5.5, 20°C DATA

Table D.1. Deposition data for pH 5.5, 20°C.

FAP	RAP	GLP	B4	B5	B6	B7	B8	TPD	MODEL	RESIDUAL
6	38	69.95	9.348	-9.6531	34.5553	-0.648	-4.332	51.1	42.95706	8.142942
33.75	32.55	63.4	45.04106	-49.21425	26.82771	-20.50313	-3.178508	6.45	12.9068	-6.456798
17.95	20.3	61.45	14.93979	-25.36963	16.21666	-5.799645	-1.23627	9.1	12.11867	-3.018673
4.7	12.5	60.5	2.40875	-6.54005	9.83125	-0.39762	-0.46875	12.1	17.91229	-5.812287
17.1	16.3	54.55	11.42793	-21.45452	11.55915	-5.26338	-0.79707	15	8.71785	6.28215
14.75	45.1	53.25	27.27423	-18.06506	31.22048	-3.916125	-6.10203	21.75	44.22054	-22.47054
11.5	8.8	52.65	4.1492	-13.92593	6.02316	-2.3805	-0.23232	0.95	6.691074	-5.741074
31.85	39.8	46.85	51.97283	-34.31997	24.24019	-18.25961	-4.75212	42.2	32.77681	9.423191
14.4	18.85	45.45	11.12904	-15.05304	11.13752	-3.73248	-1.065968	11.45	15.62521	-4.175211
16.3	26.45	40.6	17.67654	-15.22094	13.96031	-4.78242	-2.098808	27.6	22.86156	4.738442
17.3	26.4	38.95	18.72552	-15.49821	13.36764	-5.38722	-2.09088	24.2	22.44332	1.756676
14.75	18.05	37.05	10.91574	-12.56921	8.693783	-3.916125	-0.977408	11.1	15.30582	-4.205824
17.5	9.15	30.1	6.565125	-12.11525	3.580395	-5.5125	-0.251168	10.35	5.318984	5.031016
16.8	16.05	29.6	11.05524	-11.43744	6.17604	-5.08032	-0.772808	19.9	13.05895	6.841046
16.95	29.25	29.2	20.32729	-11.38362	11.1033	-5.171445	-2.566688	26.45	25.60549	0.844509
17.55	0.25	28.25	0.179888	-11.40311	0.091813	-5.544045	-0.000188	3.05	-3.703696	6.753696
7.45	21.8	27.4	6.65881	-4.69499	7.76516	-0.999045	-1.42572	24.55	20.40022	4.149782
16.8	24.05	26.9	16.56564	-10.39416	8.410285	-5.08032	-1.735208	20.3	20.97012	-0.670124
0.75	22.35	26.75	0.687263	-0.461438	7.772213	-0.010125	-1.498568	18.25	19.55331	-1.303309
26	29.45	26.5	31.3937	-15.847	10.14553	-12.168	-2.601908	19.95	24.31959	-4.369593
15.45	33.4	25.8	21.15723	-9.16803	11.20236	-4.296645	-3.34668	36.9	28.86569	8.034314
0.5	24.75	25.65	0.507375	-0.294975	8.252888	-0.0045	-1.837688	22.65	19.70971	2.940295
33.95	24.75	25.6	34.45076	-19.98976	8.2368	-20.74685	-1.837688	23.85	13.56418	10.28582
16	27.4	25.5	17.9744	-9.384	9.0831	-4.608	-2.25228	24.05	24.04501	0.00499
17.05	20.7	25.15	14.47034	-9.862573	6.767865	-5.232645	-1.28547	18.85	18.01047	0.839527
33.25	30.4	24.55	41.4428	-18.77461	9.70216	-19.90013	-2.77248	14.95	23.21204	-8.262042
8.1	23.5	23.85	7.80435	-4.443255	7.286175	-1.18098	-1.65675	24.9	20.91134	3.988661
16.55	40.8	23.7	27.68484	-9.021405	12.57048	-4.930245	-4.99392	37.8	34.74249	3.057515
15	34.2	23.6	21.033	-8.142	10.49256	-4.05	-3.50892	36.1	29.13124	6.968756
17.25	26.35	23.2	18.63604	-9.2046	7.94716	-5.356125	-2.082968	21.4	23.15401	-1.754011
15.9	0	20.45	0	-7.478565	0	-4.55058	0	-2.75	0.915431	-3.665431
13.35	17.1	20.15	9.359685	-6.187058	4.479345	-3.208005	-0.87723	13.85	16.61885	-2.768846
14.8	17.3	18.65	10.49764	-6.34846	4.194385	-3.94272	-0.89787	13.3	16.56229	-3.262288
13.2	9.6	17.55	5.19552	-5.32818	2.19024	-3.13632	-0.27648	15.15	11.6215	3.528497
22.2	77.5	17.3	70.5405	-8.83338	17.42975	-8.87112	-18.01875	71.35	66.47146	4.878544
14.85	8.85	16	5.388323	-5.4648	1.8408	-3.969405	-0.234968	6.1	10.53961	-4.43961
24.65	83.5	15.75	84.38928	-8.929463	17.09663	-10.93721	-20.91675	82.15	75.10084	7.049161
16.05	16.55	13.6	10.89073	-5.02044	2.92604	-4.636845	-0.821708	16.95	16.37684	0.573158
13.7	21.1	13.1	11.85187	-4.12781	3.59333	-3.37842	-1.33563	23.45	19.66057	3.789435
58.05	36.95	10.4	87.94285	-13.88556	4.99564	-60.65645	-4.095908	37.55	28.33096	9.219044
37.2	45.9	9.2	70.00668	-7.87152	5.48964	-24.90912	-6.32043	40.3	50.06759	-9.767589
11.05	38.15	9.15	17.28386	-2.325473	4.537943	-2.197845	-4.366268	36.5	26.13292	10.36708
37.55	15.3	8.5	23.55512	-7.341025	1.69065	-25.38005	-0.70227	4.65	5.107118	-0.457118
5.7	5.45	8.35	1.273665	-1.094685	0.591598	-0.58482	-0.089108	5.3	12.98763	-7.687632
5.35	34.15	8.1	7.490803	-0.996705	3.595995	-0.515205	-3.498668	22.2	19.18225	3.017749
11.95	40.7	7.4	19.94097	-2.03389	3.91534	-2.570445	-4.96947	39	27.50822	11.49178
45.95	52.6	7.35	99.09577	-7.767848	5.02593	-38.00525	-8.30028	64.3	64.00186	0.298144
42.95	43.9	7	77.30571	-6.91495	3.9949	-33.20465	-5.78163	39.95	49.12749	-9.177492
38.35	48.35	6.95	76.02312	-6.130248	4.368423	-26.47301	-7.013168	40.85	54.48235	-13.63235
4.1	50.45	6.7	8.480645	-0.63181	4.394195	-0.30258	-7.635608	18.35	17.61301	0.736994
3.8	52.05	5.9	8.10939	-0.51566	3.992235	-0.25992	-8.127608	10.4	16.52131	-6.121308
37.1	47.8	5.85	72.70858	-4.991805	3.63519	-24.77538	-6.85452	52.5	53.38098	-0.880979
34.35	49.2	5.15	69.29082	-4.068758	3.29394	-21.23861	-7.26192	60	53.63763	6.362368
3.4	53.9	5.05	7.51366	-0.39491	3.538535	-0.20808	-8.71563	9	15.07429	-6.074288
3.2	65.8	4.25	8.63296	-0.3128	3.63545	-0.18432	-12.98892	9.7	12.32345	-2.623451
3.45	61.15	3.95	8.649668	-0.313433	3.140053	-0.214245	-11.21797	6.05	13.49549	-7.445493
16.75	18	3.25	12.3615	-1.252063	0.7605	-5.050125	-0.972	18.55	18.85207	-0.302067
5.95	20.9	2.8	5.098555	-0.38318	0.76076	-0.637245	-1.31043	20.25	16.48251	3.767493
15.05	12.9	1.35	7.959945	-0.467303	0.226395	-4.077045	-0.49923	10.6	16.0956	-5.495601
14.8	12.7	0.6	7.70636	-0.20424	0.09906	-3.94272	-0.48387	13	16.12174	-3.121741

Table D.2. Test deposition data for pH 5.5, 20°C.

FAP	RAP	GLP	TPD
15.85	15.7	11.75	15.05
14.8	23.85	24.25	24.7
15.65	17.3	43.65	12.8
23.9	24	23.85	23.3
6.35	21.45	5.45	22.25

Modelling data for depositions at pH 5.5, 20°C

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\Liz5.5stats\liz55.SYD, created Tue Feb 18, 2003 at 18:27:40, contains variables:

FAP RAP GLP TPD

60 cases and 4 variables processed and saved.

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\Liz5.5stats\liz55respfact.SYD, created Wed Feb 19, 2003 at 14:22:13, contains variables:

FAP RAP GLP TPD

Dep Var: TPD N: 60 Multiple R: 0.933 Squared multiple R: 0.870

Adjusted squared multiple R: 0.846 Standard error of estimate: 6.882

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	10.596	6.794	0.000	.	1.560	0.125
FAP	-0.063	0.407	-0.044	0.033	-0.154	0.878
RAP	-0.013	0.211	-0.013	0.057	-0.063	0.950
GLP	0.274	0.225	0.274	0.052	1.217	0.229
FAP*FAP	-0.016	0.005	-0.559	0.070	-2.890	0.006
RAP*FAP	0.040	0.006	1.435	0.053	6.475	0.000
GLP*FAP	-0.023	0.005	-0.504	0.187	-4.273	0.000
RAP*RAP	-0.003	0.002	-0.201	0.077	-1.095	0.279
GLP*RAP	0.014	0.004	0.461	0.153	3.523	0.001
GLP*GLP	-0.005	0.003	-0.306	0.078	-1.675	0.100

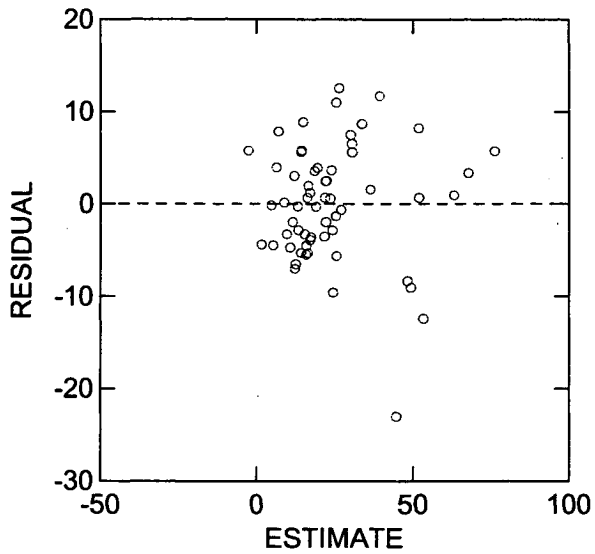
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	15802.414	9	1755.824	37.072	0.000
Residual	2368.157	50	47.363		

*** WARNING ***
Case 1 has large leverage (Leverage = 0.666)
Case 1 is an outlier (Studentized Residual = 3.197)
Case 2 has large leverage (Leverage = 0.618)
Case 6 is an outlier (Studentized Residual = -4.683)
Case 37 has large leverage (Leverage = 0.527)
Case 40 has large leverage (Leverage = 0.692)
Case 43 has large leverage (Leverage = 0.407)

Durbin-Watson D Statistic 2.225
First Order Autocorrelation -0.141

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 60 Multiple R: 0.929 Squared multiple R: 0.863

Adjusted squared multiple R: 0.842 Standard error of estimate: 6.978

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.408	0.276	0.508	0.023	1.475	0.146
RAP	0.230	0.144	0.460	0.032	1.597	0.116
GLP	0.482	0.183	0.798	0.029	2.630	0.011
FAP*FAP	-0.019	0.005	-0.865	0.055	-3.918	0.000
RAP*FAP	0.035	0.005	1.693	0.042	6.703	0.000
GLP*FAP	-0.028	0.005	-0.859	0.116	-5.655	0.000
RAP*RAP	-0.004	0.002	-0.385	0.048	-1.633	0.109
GLP*RAP	0.012	0.004	0.581	0.078	3.139	0.003
GLP*GLP	-0.006	0.003	-0.467	0.054	-2.098	0.041

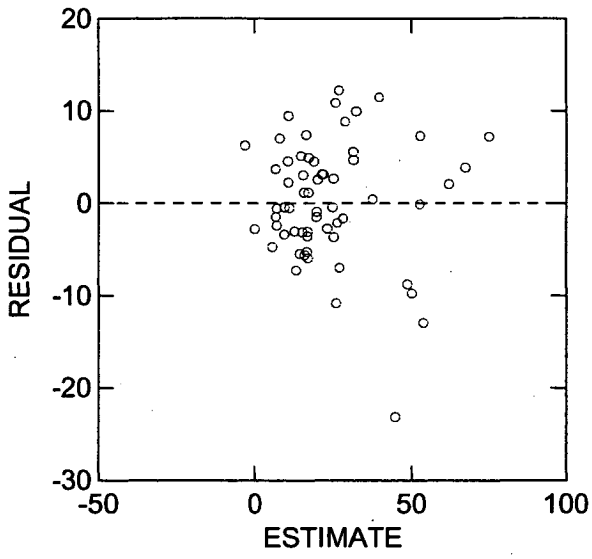
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	15687.211	8	1960.901	40.270	0.000
Residual	2483.360	51	48.693		

*** WARNING ***
Case 1 has large leverage (Leverage = 0.665)
Case 2 has large leverage (Leverage = 0.554)
Case 6 is an outlier (Studentized Residual = -4.610)
Case 37 has large leverage (Leverage = 0.509)
Case 40 has large leverage (Leverage = 0.676)

Durbin-Watson D Statistic 2.155
First Order Autocorrelation -0.105

Plot of Residuals against Predicted Values



Step # 0 R = 0.933 R-Square = 0.870

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	-0.063	0.407	-0.044	0.03259	1	0.024	0.878
3	RAP	-0.013	0.211	-0.013	0.05661	1	0.004	0.950
4	GLP	0.274	0.225	0.274	0.05155	1	1.482	0.229
5	FAP*FAP	-0.016	0.005	-0.559	0.06970	1	8.351	0.006
6	RAP*FAP	0.040	0.006	1.435	0.05307	1	41.920	0.000
7	GLP*FAP	-0.023	0.005	-0.504	0.18702	1	18.260	0.000
8	RAP*RAP	-0.003	0.002	-0.201	0.07712	1	1.198	0.279
9	GLP*RAP	0.014	0.004	0.461	0.15256	1	12.412	0.001
10	GLP*GLP	-0.005	0.003	-0.306	0.07803	1	2.807	0.100
Out		Part. Corr.						
	none							

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.933 R-Square = 0.870
Term removed: RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
	FAP							

2		-0.054	0.376	-0.037	0.03742	1	0.020	0.887
4	GLP	0.278	0.212	0.278	0.05689	1	1.721	0.195
5	FAP*FAP	-0.016	0.005	-0.563	0.07712	1	9.552	0.003
6	RAP*FAP	0.040	0.006	1.431	0.05699	1	45.676	0.000
7	GLP*FAP	-0.024	0.005	-0.506	0.19080	1	19.079	0.000
8	RAP*RAP	-0.003	0.001	-0.210	0.20504	1	3.551	0.065
9	GLP*RAP	0.014	0.004	0.457	0.19506	1	15.918	0.000
10	GLP*GLP	-0.005	0.003	-0.307	0.07816	1	2.876	0.096
Out		Part. Corr.						
3	RAP	-0.009	.	.	0.05661	1	0.004	0.950

Step # 2 R = 0.933 R-Square = 0.870
Term removed: FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
4	GLP	0.279	0.210	0.279	0.05697	1	1.771	0.189
5	FAP*FAP	-0.016	0.004	-0.579	0.13230	1	17.710	0.000
6	RAP*FAP	0.039	0.004	1.412	0.09894	1	78.620	0.000
7	GLP*FAP	-0.024	0.004	-0.515	0.29411	1	31.144	0.000
8	RAP*RAP	-0.003	0.001	-0.202	0.27888	1	4.547	0.038
9	GLP*RAP	0.014	0.004	0.459	0.20046	1	16.868	0.000
10	GLP*GLP	-0.005	0.003	-0.303	0.07945	1	2.916	0.094
Out		Part. Corr.						
2	FAP	-0.020	.	.	0.03742	1	0.020	0.887
3	RAP	-0.001	.	.	0.06500	1	0.000	0.994

Step # 3 R = 0.930 R-Square = 0.865
Term removed: GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
5	FAP*FAP	-0.017	0.004	-0.625	0.14088	1	21.602	0.000
6	RAP*FAP	0.040	0.004	1.434	0.10003	1	80.829	0.000
7	GLP*FAP	-0.022	0.004	-0.468	0.34647	1	29.769	0.000
8	RAP*RAP	-0.003	0.001	-0.247	0.31935	1	7.666	0.008
9	GLP*RAP	0.016	0.003	0.498	0.21483	1	20.930	0.000
10	GLP*GLP	-0.002	0.002	-0.110	0.23981	1	1.142	0.290
Out		Part. Corr.						
2	FAP	-0.027	.	.	0.03747	1	0.037	0.849
3	RAP	-0.051	.	.	0.07035	1	0.136	0.714
4	GLP	0.181	.	.	0.05697	1	1.771	0.189

Step # 4 R = 0.929 R-Square = 0.862
Term removed: GLP*GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
5	FAP*FAP	-0.018	0.004	-0.636	0.14173	1	22.455	0.000
6	RAP*FAP	0.041	0.004	1.469	0.10452	1	88.438	0.000
7	GLP*FAP	-0.023	0.004	-0.493	0.37486	1	35.680	0.000
8	RAP*RAP	-0.003	0.001	-0.228	0.33340	1	6.768	0.012
9	GLP*RAP	0.013	0.003	0.420	0.38890	1	26.902	0.000
Out		Part. Corr.						
2	FAP	0.014	.	.	0.04036	1	0.010	0.922
3	RAP	-0.014	.	.	0.07482	1	0.010	0.922
4	GLP	-0.015	.	.	0.17197	1	0.013	0.911
10	GLP*GLP	-0.145	.	.	0.23981	1	1.142	0.290

Dep Var: TPD N: 60 Multiple R: 0.929 Squared multiple R: 0.862

Adjusted squared multiple R: 0.850 Standard error of estimate: 6.808

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	12.865	1.610	0.000	.	7.993	0.000
FAP*FAP	-0.018	0.004	-0.636	0.142	-4.739	0.000
RAP*FAP	0.041	0.004	1.469	0.105	9.404	0.000
GLP*FAP	-0.023	0.004	-0.493	0.375	-5.973	0.000
RAP*RAP	-0.003	0.001	-0.228	0.333	-2.601	0.012
GLP*RAP	0.013	0.003	0.420	0.389	5.187	0.000

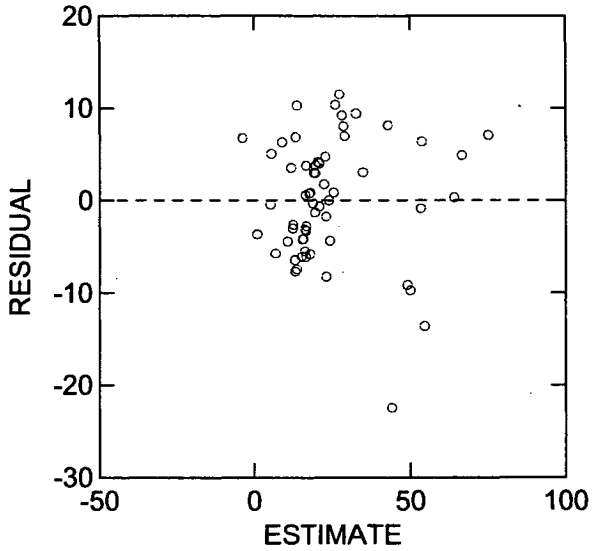
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	15667.809	5	3133.562	67.610	0.000
Residual	2502.762	54	46.347		

*** WARNING ***
Case 1 has large leverage (Leverage = 0.532)
Case 2 has large leverage (Leverage = 0.411)
Case 6 is an outlier (Studentized Residual = -4.368)
Case 37 has large leverage (Leverage = 0.342)
Case 40 has large leverage (Leverage = 0.603)

Durbin-Watson D Statistic 2.110
First Order Autocorrelation -0.070

Plot of Residuals against Predicted Values



Step # 0 R = 0.976 R-Square = 0.953

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.408	0.276	0.299	0.02263	1	2.176	0.146
2	RAP	0.230	0.144	0.271	0.03228	1	2.551	0.116
3	GLP	0.482	0.183	0.469	0.02911	1	6.914	0.011
4	FAP*FAP	-0.019	0.005	-0.509	0.05492	1	15.348	0.000
5	RAP*FAP	0.035	0.005	0.996	0.04202	1	44.931	0.000
6	GLP*FAP	-0.028	0.005	-0.505	0.11620	1	31.982	0.000
7	RAP*RAP	-0.004	0.002	-0.226	0.04818	1	2.665	0.109
8	GLP*RAP	0.012	0.004	0.342	0.07825	1	9.851	0.003
9	GLP*GLP	-0.006	0.003	-0.275	0.05412	1	4.403	0.041

Out	Part. Corr.
none	

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.975 R-Square = 0.951
Term removed: FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
2	RAP	0.319	0.132	0.376	0.03917	1	5.827	0.019
3	GLP	0.631	0.155	0.614	0.04179	1	16.631	0.000
4	FAP*FAP	-0.015	0.004	-0.395	0.08531	1	14.012	0.000

5	RAP*FAP	0.038	0.005	1.098	0.05382	1	68.465	0.000
6	GLP*FAP	-0.025	0.005	-0.451	0.13964	1	29.979	0.000
7	RAP*RAP	-0.005	0.002	-0.303	0.05607	1	5.436	0.024
8	GLP*RAP	0.010	0.004	0.286	0.08911	1	7.665	0.008
9	GLP*GLP	-0.008	0.003	-0.360	0.06739	1	9.227	0.004

Out		Part. Corr.						
1	FAP	0.202	.	.	0.02263	1	2.176	0.146

Model contains no constant

Dep Var: TPD N: 60 Multiple R: 0.975 Squared multiple R: 0.951

Adjusted squared multiple R: 0.944 Standard error of estimate: 7.057

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
RAP	0.319	0.132	0.376	0.039	2.414	0.019
GLP	0.631	0.155	0.614	0.042	4.078	0.000
FAP*FAP	-0.015	0.004	-0.395	0.085	-3.743	0.000
RAP*FAP	0.038	0.005	1.098	0.054	8.274	0.000
GLP*FAP	-0.025	0.005	-0.451	0.140	-5.475	0.000
RAP*RAP	-0.005	0.002	-0.303	0.056	-2.332	0.024
GLP*RAP	0.010	0.004	0.286	0.089	2.769	0.008
GLP*GLP	-0.008	0.003	-0.360	0.067	-3.038	0.004

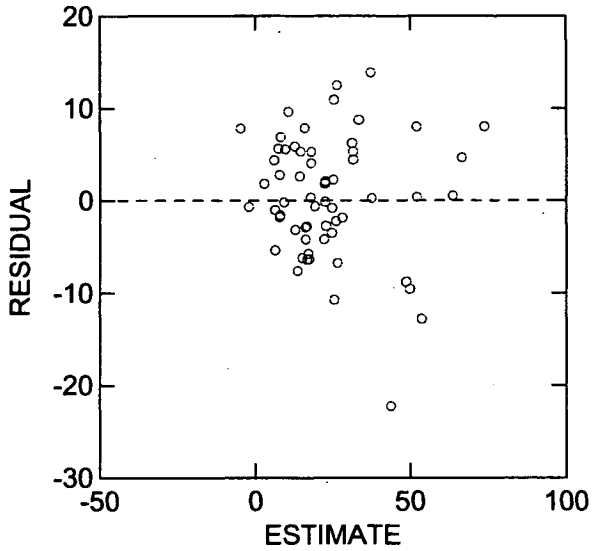
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	49939.938	8	6242.492	125.364	0.000
Residual	2589.327	52	49.795		

*** WARNING ***
Case 1 has large leverage (Leverage = 0.610)
Case 1 is an outlier (Studentized Residual = 3.468)
Case 2 has large leverage (Leverage = 0.544)
Case 6 is an outlier (Studentized Residual = -4.247)
Case 37 has large leverage (Leverage = 0.502)
Case 40 has large leverage (Leverage = 0.614)

Durbin-Watson D Statistic 2.014
First Order Autocorrelation -0.050

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 60 Multiple R: 0.926 Squared multiple R: 0.857

Adjusted squared multiple R: 0.838 Standard error of estimate: 7.057

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
RAP	0.319	0.132	0.638	0.039	2.414	0.019
GLP	0.631	0.155	1.044	0.042	4.078	0.000
FAP*FAP	-0.015	0.004	-0.671	0.085	-3.743	0.000
RAP*FAP	0.038	0.005	1.867	0.054	8.274	0.000
GLP*FAP	-0.025	0.005	-0.767	0.140	-5.475	0.000
RAP*RAP	-0.005	0.002	-0.515	0.056	-2.332	0.024
GLP*RAP	0.010	0.004	0.486	0.089	2.769	0.008
GLP*GLP	-0.008	0.003	-0.613	0.067	-3.038	0.004

Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	15581.244	7	2225.892	44.701	0.000
Residual	2589.327	52	49.795		

*** WARNING ***

Case 1 has large leverage (Leverage = 0.610)

Case 1 is an outlier (Studentized Residual = 3.468)

Case 2 has large leverage (Leverage = 0.544)

Case 6 is an outlier (Studentized Residual = -4.247)

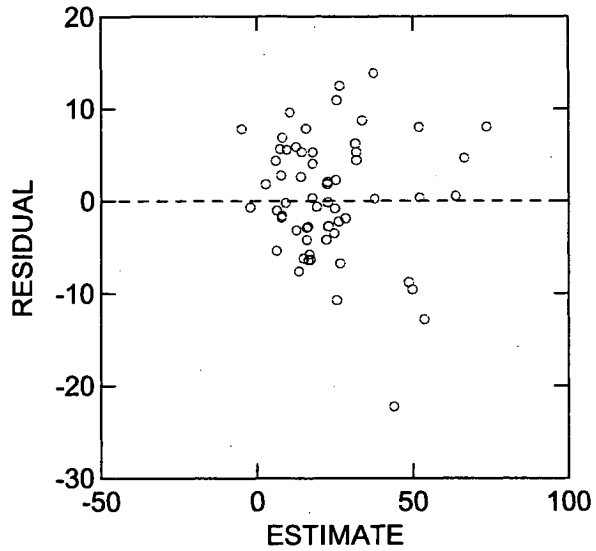
Case 37 has large leverage (Leverage = 0.502)

Case 40 has large leverage (Leverage = 0.614)

Durbin-Watson D Statistic 2.014

First Order Autocorrelation -0.050

Plot of Residuals against Predicted Values



Dep Var: TPD N: 60 Multiple R: 0.933 Squared multiple R: 0.870

Adjusted squared multiple R: 0.849 Standard error of estimate: 6.816

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	9.818	4.511	0.000	.	2.176	0.034
RAP	-0.002	0.195	-0.002	0.065	-0.008	0.994
GLP	0.279	0.220	0.279	0.053	1.265	0.212
FAP*FAP	-0.016	0.004	-0.579	0.131	-4.148	0.000
RAP*FAP	0.039	0.004	1.412	0.099	8.778	0.000
GLP*FAP	-0.024	0.004	-0.515	0.291	-5.500	0.000
RAP*RAP	-0.003	0.002	-0.201	0.077	-1.104	0.275
GLP*RAP	0.014	0.004	0.460	0.153	3.554	0.001
GLP*GLP	-0.005	0.003	-0.303	0.079	-1.685	0.098

Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	15801.289	8	1975.161	42.516	0.000
Residual	2369.282	51	46.457		

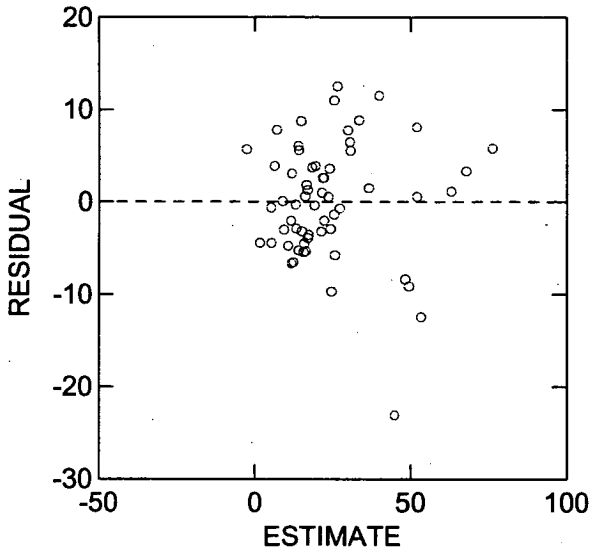
*** WARNING ***

Case	1 has large leverage	(Leverage =	0.636)
Case	2 has large leverage	(Leverage =	0.553)
Case	6 is an outlier	(Studentized Residual =	-4.728)
Case	37 has large leverage	(Leverage =	0.525)
Case	40 has large leverage	(Leverage =	0.624)

Durbin-Watson D Statistic 2.225

First Order Autocorrelation -0.140

Plot of Residuals against Predicted Values



APPENDIX E - pH 7.0, 50°C DATA

Table E.1. Deposition data for pH 7.0, 50°C.

	Jar	FAP	RAP	GLP	B1	B5	B6	B8	B9	TPD	MODEL	RESIDUAL
30-Sep-02	B	29.41	41.72	28.22	7.26427	-11.6193	-10.59605	29.58949	8.760052	27.805	28.37818	-0.573177
30-Sep-02	C	27.86	31.32	23.86	6.88142	-9.306354	-6.725657	16.67602	6.262296	28.875	18.31529	10.55971
30-Sep-02	D	50.95	33.685	23.585	12.58465	-16.82318	-7.150147	19.28955	6.118774	31.975	18.7864	13.1886
30-Sep-02	E	57.89	33.12	23.25	14.29883	-18.8432	-6.93036	18.64788	5.946188	-0.84	17.91249	-18.75249
30-Sep-02	G	28.08	33.415	22.25	6.93576	-8.74692	-6.691354	18.98156	5.445688	4.235	20.47578	-16.24078
30-Sep-02	H	35.17	35.02	37.32	8.68699	-18.37562	-11.76252	20.84881	15.32061	10.425	19.80768	-9.382678
29-Oct-02	A	20.67	5.33	0	5.10549	0	0	0.482951	0	9.075	9.314666	-0.239666
29-Oct-02	B	15.145	9.99	0	3.740815	0	0	1.696602	0	13.905	9.192264	4.712736
29-Oct-02	C	9.985	20.825	0	2.466295	0	0	7.372571	0	1.6	13.73232	-12.13232
29-Oct-02	D	10.1	30.525	0	2.4947	0	0	15.84019	0	12.825	22.43691	-9.61191
29-Oct-02	E	26.33	9.725	0	6.50351	0	0	1.607786	0	27.075	11.86652	15.20848
29-Oct-02	F	21.955	22.765	0	5.422885	0	0	8.810169	0	15.34	18.16466	-2.82466
29-Oct-02	G	22.97	26.35	0	5.67359	0	0	11.80348	0	2.175	21.48263	-19.30763
29-Oct-02	H	4.09	10.8	14.72	1.01023	-0.842867	-1.430784	1.98288	2.383462	6.47	6.948012	-0.478012
29-Oct-02	I	0	11.93	10.21	0	0	-1.096248	2.419523	1.146685	3.98	6.273109	-2.293109
29-Oct-02	J	0	30.69	8.25	0	0	-2.278733	16.01189	0.748688	8.675	18.61546	-9.94046
29-Oct-02	M	0	21.825	32.915	0	0	-6.465329	8.097621	11.91737	21.44	17.78811	3.651894
29-Oct-02	N	0	30.33	41.165	0	0	-11.23681	15.63845	18.64013	21.235	27.65716	-6.42216
29-Oct-02	Q	0	45.12	37.43	0	0	-15.19957	34.60884	15.41105	38.3	39.84107	-1.541069
1-Oct-02	B	41.03	34.07	37.875	10.13441	-21.75616	-11.61361	19.733	15.77967	16.07	17.42832	-1.358318
1-Oct-02	C	29.805	29.53	27.28	7.361835	-11.38313	-7.250206	14.82436	8.186182	6.82	16.31941	-9.499409
1-Oct-02	E	25.875	50.785	21.69	6.391125	-7.857203	-9.91374	43.84498	5.175017	36.66	42.79149	-6.131493
1-Oct-02	H	0	27.82	1.075	0	0	-0.269159	13.15719	0.012712	17.635	16.93598	0.699017
1-Oct-02	I	13.56	0.81	0.785	3.34932	-0.149024	-0.005723	0.011154	0.006778	8.275	6.929068	1.345932
1-Oct-02	J	24.74	0.28	0.78	6.11078	-0.270161	-0.001966	0.001333	0.006692	16.22	9.568302	6.651698
16-Oct-02	A	34.65	0	32.24	8.55855	-15.63962	0	0	11.43359	14.625	8.712328	5.912672
16-Oct-02	C	34.04	0	12.39	8.40788	-5.904578	0	0	1.688633	5.07	8.086008	-3.016008
16-Oct-02	D	14.39	0	13.645	3.55433	-2.748922	0	0	2.048046	0.97	6.680196	-5.710196
16-Oct-02	E	17.63	0	55.13	4.35461	-13.60719	0	0	33.43249	33.29	29.04042	4.249576
16-Oct-02	F	18.39	0	11.245	4.54233	-2.895138	0	0	1.39095	4.2615	6.852675	-2.591175
16-Oct-02	G	0	21.905	1.675	0	0	-0.330218	8.157093	0.030862	6.34	11.77058	-5.430579
16-Oct-02	H	0	33.4	50.04	0	0	-15.04202	18.96452	27.54402	30.295	36.40503	-6.110027
16-Oct-02	I	30.485	20.18	0.525	7.529795	-0.224065	-0.095351	6.922951	0.003032	26.93	18.02908	8.900921
16-Oct-02	K	20.665	0	0	5.104255	0	0	0	0	9.105	8.818584	0.286416
16-Oct-02	L	29.575	0	1.33	7.305025	-0.550687	0	0	0.019458	9.505	10.50319	-0.998191
16-Oct-02	M	20.305	0	0.48	5.015335	-0.13645	0	0	0.002534	8.635	8.598836	0.036164
16-Oct-02	N	2.195	0	6.745	0.542165	-0.207274	0	0	0.500445	2.005	4.562678	-2.557678
16-Oct-02	Q	1.74	0	15.02	0.42978	-0.365887	0	0	2.481604	0.42	6.325954	-5.905954
11-Jun-02	B	1.44	26.775	2.2	0.35568	-0.044352	-0.530145	12.18731	0.05324	16.435	16.03669	0.398308
11-Jun-02	D	1.675	24.95	8.35	0.413725	-0.195808	-1.874993	10.58254	0.766948	19.1	13.69567	5.404328
11-Jun-02	E	2.23	28.29	20.755	0.55081	-0.647971	-5.284431	13.60551	4.73847	20.925	17.16632	3.758685
11-Jun-02	F	2.53	24.755	1.415	0.62491	-0.050119	-0.315255	10.41777	0.022024	21.575	14.66928	6.905723
11-Jun-02	G	2.66	24.955	2.195	0.65702	-0.081742	-0.492986	10.58678	0.052998	14.77	14.69856	0.071439
11-Jun-02	H	2.85	21.24	5.455	0.70395	-0.217655	-1.042778	7.669339	0.327327	15.84	11.35746	4.482539
11-Jun-02	I	2.94	20.075	9.41	0.72618	-0.387316	-1.700152	6.851096	0.974029	14.55	10.38419	4.165809
11-Jun-02	J	3.685	23.135	18.685	0.910195	-0.963959	-3.890497	9.09888	3.840421	17.38	13.06633	4.313671
11-Jun-02	K	3.764	26.354	1.26	0.929708	-0.066397	-0.298854	11.80707	0.017464	19.068	16.39361	2.67439
11-Jun-02	L	2.805	17.875	1.74	0.692835	-0.06833	-0.279923	5.431766	0.033304	7.735	9.657391	-1.922391
11-Jun-02	M	4.01	19.665	12.345	0.99047	-0.693048	-2.18488	6.574108	1.676389	12.61	10.30369	2.306313
11-Jun-02	N	3.135	16.37	4.68	0.774345	-0.205405	-0.689504	4.555607	0.240926	9.55	8.512489	1.037511
11-Jun-02	Q	3.765	17.69	15.03	0.929955	-0.792231	-2.392926	5.319914	2.48491	10.93	9.482825	1.447175
1-Jun-02	A	24.211	39.234	9.771	5.980117	-3.31192	-3.450199	26.16821	1.050197	44.521	30.91426	13.60674
1-Jun-02	B	26.665	41.29	9.27	6.586255	-3.460584	-3.444825	28.98269	0.945262	25.5	34.15726	-8.657256
1-Jun-02	C	25.165	36.27	15.595	6.215755	-5.494274	-5.090676	22.36372	2.675244	23.025	25.15237	-2.127367
1-Jun-02	D	27.5	42.76	22.84	6.7925	-8.7934	-8.789746	31.0831	5.738322	49.405	30.89818	18.50682
1-Jun-02	E	24.625	44.34	39.91	6.082375	-13.75897	-15.92648	33.42261	17.52089	44.83	32.70707	12.12293
1-Jun-02	L	38.7	38.7	26.835	9.5589	-14.5392	-9.346631	25.46073	7.921289	28.815	23.97471	4.840295
1-Jun-02	M	13.105	29.545	8.42	3.236935	-1.544817	-2.23892	14.83942	0.77986	20.39	19.21597	1.17403
1-Jun-02	N	5.85	39.44	24.885	1.44495	-2.038082	-8.83318	26.44373	6.811895	32.185	28.45084	3.734164
1-Jun-02	Q	7.345	33.6	7.545	1.814215	-0.775852	-2.281608	19.19232	0.626197	28.205	22.8035	5.401497

Table E.2. Test deposition data for pH 7.0, 50°C.

	Jar	FAP	RAP	GLP	TPD
30-Sep-02	A	7.54	38.345	20.325	18.54
30-Sep-02	F	17.21	29.39	9.57	11.98
1-Oct-02	A	34.235	18.56	35.15	17.67
11-Jun-02	A	1.382	27.846	1.097	22.245
1-Jun-02	K	15.567	37.203	37.643	37.868

Modelling data for depositions at pH 7.0, 50°C

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\pH7stats\raw7.SYD, created Thu Feb 20, 2003 at 14:14:10, contains variables:

FAP RAP GLP TPD

60 cases and 4 variables processed and saved.

SYSTAT Rectangular file C:\Documents and Settings\Administrator\My Documents\Thesis\pH7stats\7respfact.SYD, created Thu Feb 20, 2003 at 14:20:39, contains variables:

FAP RAP GLP TPD

Dep Var: TPD N: 60 Multiple R: 0.778 Squared multiple R: 0.605

Adjusted squared multiple R: 0.533 Standard error of estimate: 8.164

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	1.021	5.121	0.000	.	0.199	0.843
FAP	0.541	0.272	0.651	0.074	1.988	0.052
RAP	0.073	0.296	0.088	0.062	0.247	0.806
GLP	0.063	0.327	0.075	0.052	0.193	0.848
FAP*FAP	-0.006	0.005	-0.328	0.096	-1.141	0.259
RAP*FAP	-0.005	0.007	-0.212	0.073	-0.644	0.522
GLP*FAP	-0.010	0.007	-0.356	0.121	-1.393	0.170
RAP*RAP	0.017	0.007	0.889	0.063	2.506	0.016
GLP*RAP	-0.008	0.006	-0.327	0.131	-1.330	0.189
GLP*GLP	0.009	0.005	0.459	0.094	1.584	0.119

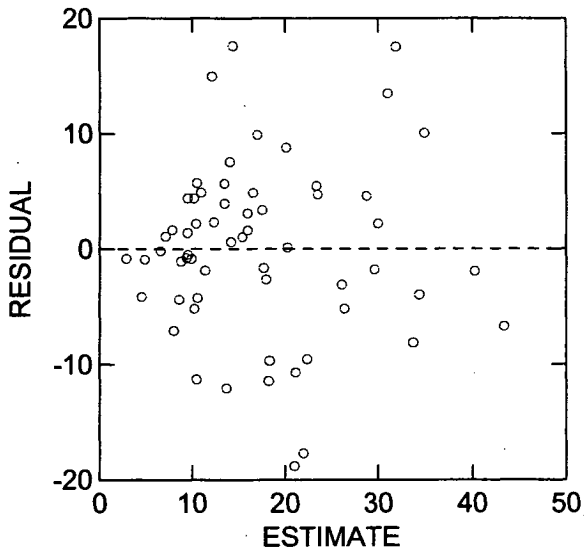
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	5093.580	9	565.953	8.492	0.000
Residual	3332.138	50	66.643		

*** WARNING ***
Case 4 has large leverage (Leverage = 0.614)
Case 26 has large leverage (Leverage = 0.481)
Case 29 has large leverage (Leverage = 0.834)
Case 32 has large leverage (Leverage = 0.447)

Durbin-Watson D Statistic 1.680
First Order Autocorrelation 0.156

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 60 Multiple R: 0.777 Squared multiple R: 0.604

Adjusted squared multiple R: 0.542 Standard error of estimate: 8.086

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.582	0.174	1.047	0.079	3.338	0.002
RAP	0.119	0.186	0.266	0.045	0.637	0.527
GLP	0.097	0.279	0.164	0.035	0.346	0.731
FAP*FAP	-0.006	0.005	-0.421	0.068	-1.246	0.218
RAP*FAP	-0.006	0.006	-0.301	0.063	-0.860	0.394
GLP*FAP	-0.010	0.007	-0.436	0.091	-1.489	0.143
RAP*RAP	0.016	0.006	1.299	0.033	2.687	0.010
GLP*RAP	-0.008	0.005	-0.434	0.089	-1.467	0.148
GLP*GLP	0.008	0.005	0.520	0.077	1.641	0.107

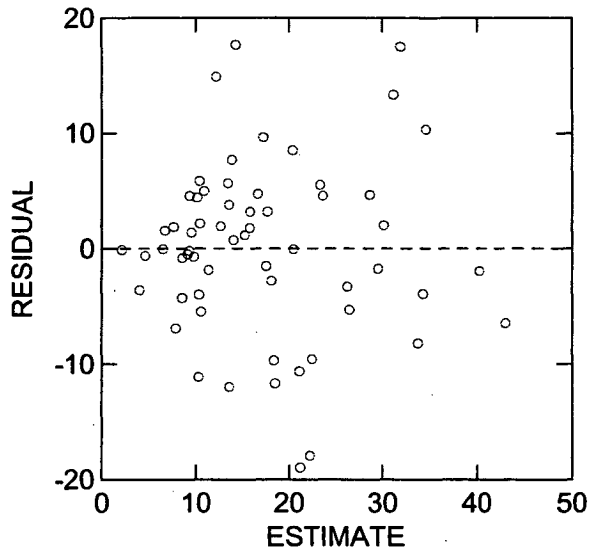
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	5090.930	8	636.366	9.732	0.000
Residual	3334.788	51	65.388		

*** WARNING ***
Case 4 has large leverage (Leverage = 0.602)
Case 19 has large leverage (Leverage = 0.402)
Case 26 has large leverage (Leverage = 0.426)
Case 29 has large leverage (Leverage = 0.832)
Case 32 has large leverage (Leverage = 0.447)

Durbin-Watson D Statistic 1.681
First Order Autocorrelation 0.156

Plot of Residuals against Predicted Values



Step # 0 R = 0.778 R-Square = 0.605

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.541	0.272	0.651	0 .07376	1	3.951	0.052
3	RAP	0.073	0.296	0.088	0 .06155	1	0.061	0.806
4	GLP	0.063	0.327	0.075	0 .05222	1	0.037	0.848
5	FAP*FAP	-0.006	0.005	-0.328	0 .09596	1	1.302	0.259
6	RAP*FAP	-0.005	0.007	-0.212	0 .07335	1	0.415	0.522
7	GLP*FAP	-0.010	0.007	-0.356	0 .12097	1	1.941	0.170
8	RAP*RAP	0.017	0.007	0.889	0 .06292	1	6.281	0.016
9	GLP*RAP	-0.008	0.006	-0.327	0 .13098	1	1.770	0.189
10	GLP*GLP	0.009	0.005	0.459	0 .09440	1	2.509	0.119
Out		Part. Corr.						
	none							

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.777 R-Square = 0.604
Term removed: GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
	FAP				0			

2		0.526	0.259	0.634	.07967 0	1	4.123	0.048
3	RAP	0.063	0.289	0.076	.06362 0	1	0.047	0.829
5	FAP*FAP	-0.006	0.005	-0.323	.09673 0	1	1.297	0.260
6	RAP*FAP	-0.005	0.007	-0.214	.07344 0	1	0.432	0.514
7	GLP*FAP	-0.009	0.006	-0.333	.15680 0	1	2.235	0.141
8	RAP*RAP	0.017	0.007	0.896	.06365 0	1	6.584	0.013
9	GLP*RAP	-0.007	0.005	-0.304	.17296 0	1	2.054	0.158
10	GLP*GLP	0.009	0.003	0.504	.26875 0	1	8.781	0.005
Out		Part. Corr.						
4	GLP	0.027	.	.	.05222 0	1	0.037	0.848

Step # 2 R = 0.777 R-Square = 0.604
Term removed: RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.495	0.213	0.596	0.11607	1	5.406	0.024
5	FAP*FAP	-0.006	0.005	-0.307	0.10349	1	1.279	0.263
6	RAP*FAP	-0.004	0.007	-0.183	0.09076	1	0.399	0.531
7	GLP*FAP	-0.009	0.006	-0.339	0.15967	1	2.410	0.127
8	RAP*RAP	0.018	0.004	0.956	0.16744	1	20.077	0.000
9	GLP*RAP	-0.007	0.005	-0.306	0.17329	1	2.124	0.151
10	GLP*GLP	0.010	0.003	0.504	0.26891	1	8.982	0.004
Out		Part. Corr.						
3	RAP	0.030	.	.	0.06362	1	0.047	0.829
4	GLP	0.021	.	.	0.05398	1	0.023	0.879

Step # 3 R = 0.775 R-Square = 0.601
Term removed: RAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.460	0.204	0.553	0.12460	1	5.066	0.029
5	FAP*FAP	-0.007	0.005	-0.352	0.11114	1	1.826	0.182
7	GLP*FAP	-0.011	0.006	-0.393	0.18907	1	3.887	0.054
8	RAP*RAP	0.017	0.003	0.869	0.28834	1	28.880	0.000
9	GLP*RAP	-0.007	0.005	-0.313	0.17384	1	2.261	0.139
10	GLP*GLP	0.010	0.003	0.543	0.30900	1	12.084	0.001
Out		Part. Corr.						
3	RAP	-0.011	.	.	0.07863	1	0.006	0.938
4	GLP	0.032	.	.	0.05481	1	0.053	0.819
6	RAP*FAP	-0.087	.	.	0.09076	1	0.399	0.531

Step # 4 R = 0.766 R-Square = 0.587
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.247	0.131	0.298	0.30574	1	3.541	0.065
7	GLP*FAP	-0.014	0.005	-0.489	0.21600	1	6.747	0.012
8	RAP*RAP	0.017	0.003	0.914	0.30126	1	32.897	0.000
9	GLP*RAP	-0.009	0.005	-0.380	0.18416	1	3.470	0.068
10	GLP*GLP	0.011	0.003	0.598	0.33207	1	15.546	0.000
Out		Part. Corr.						
3	RAP	-0.073	.	.	0.08911	1	0.281	0.598
4	GLP	0.029	.	.	0.05482	1	0.046	0.831
5	FAP*FAP	-0.183	.	.	0.11114	1	1.826	0.182
6	RAP*FAP	-0.131	.	.	0.09748	1	0.920	0.342

Step # 5 R = 0.749 R-Square = 0.561
Term removed: GLP*RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	0.244	0.134	0.293	0.30581	1	3.292	0.075
7	GLP*FAP	-0.014	0.005	-0.498	0.21613	1	6.696	0.012
8	RAP*RAP	0.013	0.002	0.678	0.82141	1	47.204	0.000
10	GLP*GLP	0.008	0.002	0.421	0.54834	1	12.151	0.001
Out		Part. Corr.						
3	RAP	-0.087	.	.	0.08954	1	0.414	0.523
4	GLP	-0.098	.	.	0.07286	1	0.519	0.474
5	FAP*FAP	-0.230	.	.	0.11774	1	3.018	0.088
6	RAP*FAP	-0.155	.	.	0.09887	1	1.328	0.254
9	GLP*RAP	-0.246	.	.	0.18416	1	3.470	0.068

Step # 6 R = 0.731 R-Square = 0.534
Term removed: FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
7	GLP*FAP	-0.006	0.003	-0.211	0.66551	1	3.557	0.064
8	RAP*RAP	0.013	0.002	0.664	0.82603	1	43.820	0.000
10	GLP*GLP	0.006	0.002	0.315	0.71475	1	8.533	0.005
Out		Part. Corr.						
2	FAP RAP	0.238	.	.	0.30581	1	3.292	0.075

3		-0.156	.	.	0.09973	1	1.376	0.246
4	GLP	-0.164	.	.	0.08064	1	1.518	0.223
5	FAP*FAP	0.036	.	.	0.28030	1	0.072	0.790
6	RAP*FAP	0.017	.	.	0.15052	1	0.016	0.899
9	GLP*RAP	-0.235	.	.	0.18420	1	3.220	0.078

Step # 7 R = 0.710 R-Square = 0.505
Term removed: GLP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
8	RAP*RAP	0.012	0.002	0.609	0.90289	1	38.536	0.000
10	GLP*GLP	0.004	0.002	0.222	0.90289	1	5.131	0.027
Out		Part. Corr.						
2	FAP	-0.069	.	.	0.94163	1	0.272	0.604
3	RAP	-0.113	.	.	0.10202	1	0.726	0.398
4	GLP	-0.244	.	.	0.09626	1	3.543	0.065
5	FAP*FAP	-0.185	.	.	0.92963	1	1.985	0.164
6	RAP*FAP	-0.199	.	.	0.54257	1	2.308	0.134
7	GLP*FAP	-0.244	.	.	0.66551	1	3.557	0.064
9	GLP*RAP	-0.243	.	.	0.18498	1	3.528	0.066

Dep Var: TPD N: 60 Multiple R: 0.710 Squared multiple R: 0.505

Adjusted squared multiple R: 0.487 Standard error of estimate: 8.557

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	7.376	1.704	0.000	.	4.330	0.000
RAP*RAP	0.012	0.002	0.609	0.903	6.208	0.000
GLP*GLP	0.004	0.002	0.222	0.903	2.265	0.027

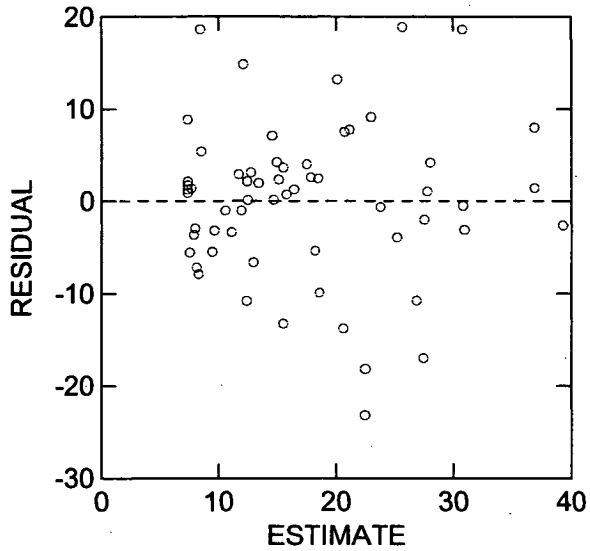
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	4252.035	2	2126.017	29.035	0.000
Residual	4173.683	57	73.223		

*** WARNING ***
Case 29 has large leverage (Leverage = 0.419)

Durbin-Watson D Statistic 1.581
First Order Autocorrelation 0.202

Plot of Residuals against Predicted Values



Step # 0 R = 0.934 R-Square = 0.873

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.582	0.174	0.593	0.07889	1	11.143	0.002
2	RAP	0.119	0.186	0.151	0.04450	1	0.406	0.527
3	GLP	0.097	0.279	0.093	0.03462	1	0.120	0.731
4	FAP*FAP	-0.006	0.005	-0.238	0.06813	1	1.554	0.218
5	RAP*FAP	-0.006	0.006	-0.170	0.06345	1	0.740	0.394
6	GLP*FAP	-0.010	0.007	-0.247	0.09058	1	2.216	0.143
7	RAP*RAP	0.016	0.006	0.735	0.03322	1	7.223	0.010
8	GLP*RAP	-0.008	0.005	-0.246	0.08884	1	2.153	0.148
9	GLP*GLP	0.008	0.005	0.294	0.07726	1	2.692	0.107
Out		Part. Corr.						
	none							

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.934 R-Square = 0.873
Term removed: GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.595	0.169	0.606	0.08249	1	12.373	0.001
2	RAP	0.144	0.170	0.183	0.05258	1	0.718	0.401
4	FAP*FAP	-0.006	0.005	-0.242	0.06832	1	1.631	0.207

5	RAP*FAP	-0.006	0.006	-0.196	0.07412	1	1.169	0.285
6	GLP*FAP	-0.009	0.006	-0.222	0.11166	1	2.246	0.140
7	RAP*RAP	0.016	0.006	0.723	0.03382	1	7.225	0.010
8	GLP*RAP	-0.007	0.005	-0.221	0.10753	1	2.155	0.148
9	GLP*GLP	0.010	0.003	0.342	0.19132	1	9.169	0.004
Out		Part. Corr.						
3	GLP	0.048	.	.	0.03462	1	0.120	0.731

Step # 2 R = 0.933 R-Square = 0.871
Term removed: RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.612	0.167	0.623	0.08366	1	13.342	0.001
4	FAP*FAP	-0.006	0.005	-0.226	0.06895	1	1.452	0.234
5	RAP*FAP	-0.007	0.006	-0.209	0.07461	1	1.337	0.253
6	GLP*FAP	-0.010	0.006	-0.245	0.11577	1	2.866	0.096
7	RAP*RAP	0.020	0.003	0.913	0.11120	1	38.099	0.000
8	GLP*RAP	-0.008	0.005	-0.241	0.11003	1	2.619	0.112
9	GLP*GLP	0.010	0.003	0.357	0.19586	1	10.258	0.002
Out		Part. Corr.						
2	RAP	0.117	.	.	0.05258	1	0.718	0.401
3	GLP	0.090	.	.	0.04090	1	0.424	0.518

Step # 3 R = 0.932 R-Square = 0.868
Term removed: RAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.616	0.168	0.627	0.08369	1	13.439	0.001
4	FAP*FAP	-0.008	0.005	-0.299	0.07754	1	2.825	0.099
6	GLP*FAP	-0.014	0.005	-0.332	0.15743	1	7.075	0.010
7	RAP*RAP	0.018	0.003	0.822	0.15495	1	42.775	0.000
8	GLP*RAP	-0.009	0.005	-0.265	0.11230	1	3.225	0.078
9	GLP*GLP	0.012	0.003	0.421	0.25988	1	18.810	0.000
Out		Part. Corr.						
2	RAP	0.128	.	.	0.05292	1	0.877	0.353
3	GLP	0.142	.	.	0.04779	1	1.087	0.302
5	RAP*FAP	-0.157	.	.	0.07461	1	1.337	0.253

Step # 4 R = 0.928 R-Square = 0.861
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	0.389	0.101	0.396	0.23692	1	14.674	0.000
	GLP*FAP							

6		-0.018	0.005	-0.434	0.20645	1	15.360	0.000
7	RAP*RAP	0.020	0.003	0.895	0.17598	1	55.748	0.000
8	GLP*RAP	-0.011	0.005	-0.339	0.12307	1	5.576	0.022
9	GLP*GLP	0.014	0.003	0.485	0.30807	1	28.703	0.000

Out		Part. Corr.						
2	RAP	0.108	.	.	0.05320	1	0.635	0.429
3	GLP	0.169	.	.	0.04879	1	1.580	0.214
4	FAP*FAP	-0.223	.	.	0.07754	1	2.825	0.099
5	RAP*FAP	-0.218	.	.	0.08391	1	2.706	0.106

Model contains no constant

Dep Var: TPD N: 60 Multiple R: 0.928 Squared multiple R: 0.861

Adjusted squared multiple R: 0.851 Standard error of estimate: 8.153

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.389	0.101	0.396	0.237	3.831	0.000
GLP*FAP	-0.018	0.005	-0.434	0.206	-3.919	0.000
RAP*RAP	0.020	0.003	0.895	0.176	7.466	0.000
GLP*RAP	-0.011	0.005	-0.339	0.123	-2.361	0.022
GLP*GLP	0.014	0.003	0.485	0.308	5.358	0.000

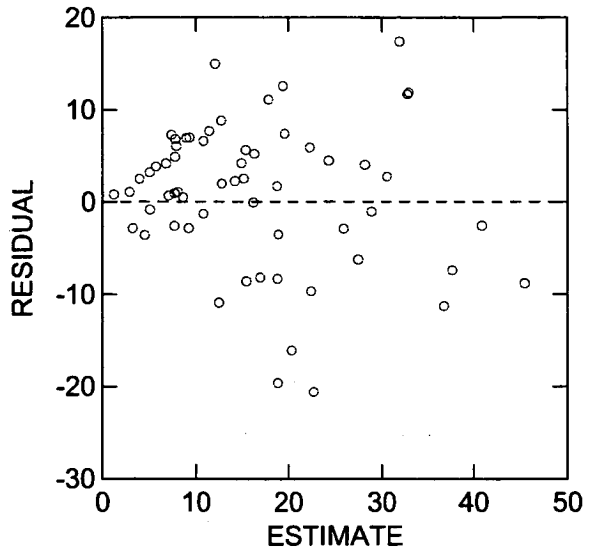
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	22625.032	5	4525.006	68.073	0.000
Residual	3656.006	55	66.473		

*** WARNING ***
Case 29 has large leverage (Leverage = 0.797)
Case 32 has large leverage (Leverage = 0.389)

Durbin-Watson D Statistic 1.605
First Order Autocorrelation 0.193

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 60 Multiple R: 0.752 Squared multiple R: 0.566

Adjusted squared multiple R: 0.535 Standard error of estimate: 8.153

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	0.389	0.101	0.699	0.237	3.831	0.000
GLP*FAP	-0.018	0.005	-0.766	0.206	-3.919	0.000
RAP*RAP	0.020	0.003	1.581	0.176	7.466	0.000
GLP*RAP	-0.011	0.005	-0.598	0.123	-2.361	0.022
GLP*GLP	0.014	0.003	0.857	0.308	5.358	0.000

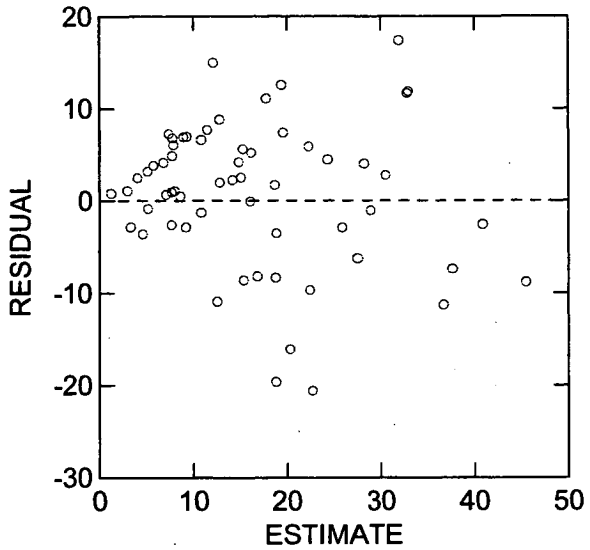
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	4769.712	4	1192.428	17.939	0.000
Residual	3656.006	55	66.473		

*** WARNING ***
Case 29 has large leverage (Leverage = 0.797)
Case 32 has large leverage (Leverage = 0.389)

Durbin-Watson D Statistic 1.605
First Order Autocorrelation 0.193

Plot of Residuals against Predicted Values



Dep Var: TPD N: 60 Multiple R: 0.766 Squared multiple R: 0.587

Adjusted squared multiple R: 0.549 Standard error of estimate: 8.027

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	3.710	2.239	0.000	.	1.657	0.103
FAP	0.247	0.131	0.298	0.306	1.882	0.065
GLP*FAP	-0.014	0.005	-0.489	0.216	-2.597	0.012
RAP*RAP	0.017	0.003	0.914	0.301	5.736	0.000
GLP*RAP	-0.009	0.005	-0.380	0.184	-1.863	0.068
GLP*GLP	0.011	0.003	0.598	0.332	3.943	0.000

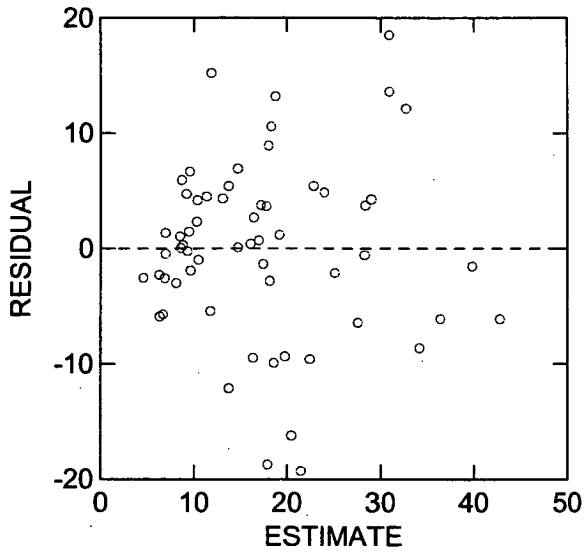
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	4946.520	5	989.304	15.355	0.000
Residual	3479.197	54	64.430		

*** WARNING ***
Case 29 has large leverage (Leverage = 0.810)
Case 32 has large leverage (Leverage = 0.398)

Durbin-Watson D Statistic 1.630
First Order Autocorrelation 0.181

Plot of Residuals against Predicted Values



APPENDIX F - pH 7.0, 20°C DATA

Table F.1. Deposition data for pH 7.0, 20°C.

FAP	RAP	GLP	B1	B2	B3	B6	B9	TPD	MODEL	RESIDUAL
18.95	22.85	27.5	22.5884	25.66055	-35.09	-32.6755	80.91875	64.2	61.53534	2.664663
23.45	30.2	25.15	27.9524	33.9146	-32.0914	-39.49556	67.67991	67.95	58.07076	9.879245
19.95	43.65	39.7	23.7804	49.01895	-50.6572	-90.11106	168.6416	92.95	100.9471	-7.99707
12.7	26.2	26.6	15.1384	29.4226	-33.9416	-36.23984	75.70892	56.95	50.21554	6.734462
6.3	8	5.8	7.5096	8.984	-7.4008	-2.4128	3.59948	16.4	10.28675	6.113252
39.95	18	7.85	47.6204	20.214	-10.0166	-7.3476	6.593608	50.55	57.06711	-6.517105
37.3	15.65	7.8	44.4616	17.57495	-9.9528	-6.34764	6.50988	46.8	52.24957	-5.449568
7.65	36.45	6.3	9.1188	40.93335	-8.0388	-11.94102	4.24683	39.15	34.33305	4.816945
7.2	33.45	6.25	8.5824	37.56435	-7.975	-10.87125	4.179688	26.7	31.4935	-4.793497
38.5	53.7	8.7	45.892	60.3051	-11.1012	-24.29388	8.09883	85.7	78.91409	6.78591
7.8	68.1	5.15	9.2976	76.4763	-6.5714	-18.23718	2.837908	63.6	63.82151	-0.221506
5.25	42.25	3.95	6.258	47.44675	-5.0402	-8.67815	1.669468	37.15	41.6675	-4.517503
11.35	29.65	5.35	13.5292	33.29695	-6.8266	-8.24863	3.062608	36.8	34.82274	1.977259
4	39.3	3.65	4.768	44.1339	-4.6574	-7.45914	1.425508	43.3	38.22185	5.078149
3.2	26.75	14.45	3.8144	30.04025	-18.4382	-20.09995	22.34187	16.15	17.70187	-1.551872
3.65	29	16.9	4.3508	32.567	-21.5644	-25.4852	30.56027	17.3	20.48561	-3.185606
2	15.4	8.2	2.384	17.2942	-10.4632	-6.56656	7.19468	7.7	9.859685	-2.159685
4.9	39.85	21.3	5.8408	44.75155	-27.1788	-44.13786	48.54483	29.2	27.9077	1.292298
6.5	54	29.25	7.748	60.642	-37.323	-82.134	91.54519	45.85	40.63468	5.215322
4.45	34.75	15.95	5.3044	39.02425	-20.3522	-28.82165	27.22107	6.8	22.42813	-15.62813
2.15	13.75	4.95	2.5628	15.44125	-6.3162	-3.53925	2.621768	4.4	10.77847	-6.378472

Table F.2. Test deposition data for pH 7.0, 20°C.

FAP	RAP	GLP	TPD
26.55	33.4	43.8	91.85
5.75	9	5.5	14
36.45	47.05	7.9	81.35
12.15	27.35	5.25	35.8
2.3	14.35	4.65	2.7

Modelling data for depositions at pH 7.0, 20°C

Dep Var: TPD N: 21 Multiple R: 0.980 Squared multiple R: 0.961

Adjusted squared multiple R: 0.929 Standard error of estimate: 6.705

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	-4.476	9.305	0.000	.	-0.481	0.640
FAP	2.768	1.112	1.356	0.012	2.490	0.030
RAP	0.702	0.467	0.416	0.046	1.501	0.162
GLP	-0.763	0.661	-0.318	0.047	-1.156	0.272
FAP*FAP	-0.043	0.023	-0.888	0.016	-1.897	0.084
RAP*FAP	0.010	0.008	0.188	0.155	1.238	0.241
GLP*FAP	-0.005	0.042	-0.043	0.026	-0.117	0.909
RAP*RAP	0.003	0.006	0.144	0.055	0.568	0.582
GLP*RAP	-0.042	0.020	-0.767	0.027	-2.102	0.059
GLP*GLP	0.079	0.032	1.267	0.013	2.453	0.032

Analysis of Variance

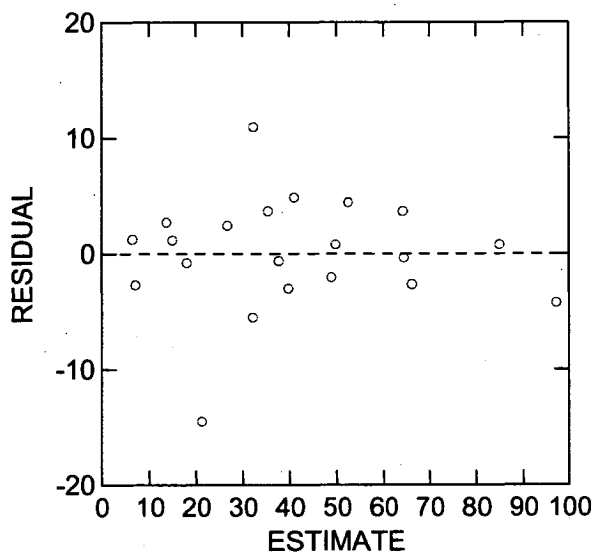
Source	Sum-of-Squares	df	Mean-Square	F-ratio	P

Regression	12166.423	9	1351.825	30.070	0.000
Residual	494.519	11	44.956		

*** WARNING ***
Case 2 has large leverage (Leverage = 0.880)
Case 3 has large leverage (Leverage = 0.883)
Case 10 has large leverage (Leverage = 0.984)
Case 10 has large influence (Cook distance = 5.093)
Case 11 has large leverage (Leverage = 0.934)
Case 20 is an outlier (Studentized Residual = -3.307)

Durbin-Watson D Statistic 2.358
First Order Autocorrelation -0.187

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 21 Multiple R: 0.980 Squared multiple R: 0.960

Adjusted squared multiple R: 0.934 Standard error of estimate: 6.487

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	2.573	1.001	1.835	0.007	2.569	0.025
RAP	0.543	0.321	0.786	0.015	1.692	0.116
GLP	-0.893	0.583	-0.626	0.020	-1.531	0.152
FAP*FAP	-0.041	0.021	-0.979	0.012	-1.898	0.082
RAP*FAP	0.011	0.008	0.270	0.086	1.374	0.194
GLP*FAP	0.001	0.039	0.013	0.016	0.029	0.977
RAP*RAP	0.005	0.005	0.325	0.034	1.036	0.321
GLP*RAP	-0.039	0.018	-1.036	0.014	-2.119	0.056
GLP*GLP	0.078	0.031	1.559	0.009	2.504	0.028

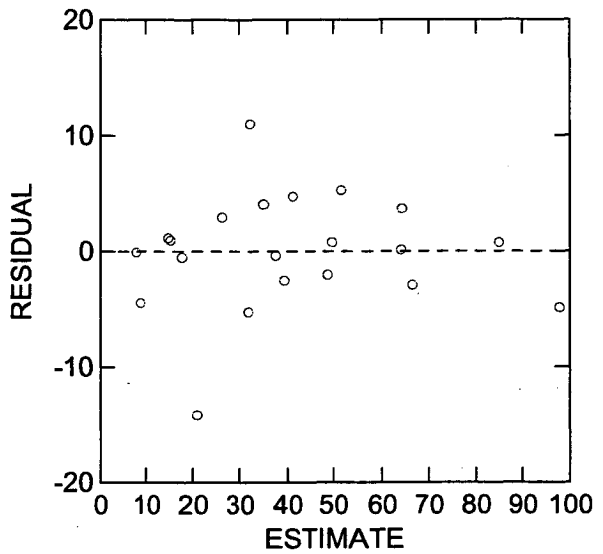
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	12156.022	8	1519.503	36.113	0.000
Residual	504.919	12	42.077		

*** WARNING ***
Case 2 has large leverage (Leverage = 0.880)
Case 3 has large leverage (Leverage = 0.841)
Case 10 has large leverage (Leverage = 0.984)
Case 10 has large influence (Cook distance = 5.449)
Case 11 has large leverage (Leverage = 0.926)
Case 20 is an outlier (Studentized Residual = -3.214)

Durbin-Watson D Statistic 2.271
First Order Autocorrelation -0.155

Plot of Residuals against Predicted Values



Step # 0 R = 0.980 R-Square = 0.961

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	2.768	1.112	1.356	.011970	1	6.198	0.030
3	RAP	0.702	0.467	0.416	.046250	1	2.253	0.162
4	GLP	-0.763	0.661	-0.318	.047020	1	1.335	0.272
5	FAP*FAP	-0.043	0.023	-0.888	.016200	1	3.600	0.084
6	RAP*FAP	0.010	0.008	0.188	.154530	1	1.533	0.241
7	GLP*FAP	-0.005	0.042	-0.043	.025840	1	0.014	0.909
8	RAP*RAP	0.003	0.006	0.144	.054820	1	0.322	0.582
9	GLP*RAP	-0.042	0.020	-0.767	.026680	1	4.417	0.059
10	GLP*GLP	0.079	0.032	1.267	.013310	1	6.016	0.032

Out		Part. Corr.
	none	

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.980 R-Square = 0.961
Term removed: GLP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	2.691	0.860	1.319	0.01834	1	9.783	0.009
3	RAP	0.699	0.447	0.414	0.04638	1	2.441	0.144
4	GLP	-0.772	0.629	-0.321	0.04764	1	1.508	0.243
5	FAP*FAP	-0.042	0.020	-0.868	0.01886	1	4.357	0.059
6	RAP*FAP	0.010	0.007	0.180	0.18560	1	1.854	0.198
8	RAP*RAP	0.003	0.005	0.146	0.05492	1	0.358	0.561
9	GLP*RAP	-0.040	0.016	-0.742	0.03968	1	6.707	0.024
10	GLP*GLP	0.076	0.019	1.220	0.03343	1	15.266	0.002
Out		Part. Corr.						
7	GLP*FAP	-0.035	.	.	0.02584	1	0.014	0.909

Step # 2 R = 0.980 R-Square = 0.960
Term removed: RAP*RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	2.680	0.839	1.313	0.01834	1	10.211	0.007
3	RAP	0.935	0.203	0.555	0.21459	1	21.303	0.000
4	GLP	-0.855	0.598	-0.356	0.05008	1	2.046	0.176
5	FAP*FAP	-0.042	0.020	-0.857	0.01889	1	4.483	0.054
6	RAP*FAP	0.010	0.007	0.179	0.18563	1	1.929	0.188
9	GLP*RAP	-0.040	0.015	-0.734	0.03976	1	6.922	0.021
10	GLP*GLP	0.077	0.019	1.238	0.03373	1	16.677	0.001
Out		Part. Corr.						
7	GLP*FAP	-0.042	.	.	0.02589	1	0.021	0.887
8	RAP*RAP	0.170	.	.	0.05492	1	0.358	0.561

Step # 3 R = 0.977 R-Square = 0.954
Term removed: RAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	2.846	0.857	1.394	0.01872	1	11.022	0.005
3	RAP	1.082	0.179	0.642	0.29497	1	36.764	0.000

4	GLP	-0.874	0.617	-0.364	0.05010	1	2.006	0.178
5	FAP*FAP	-0.039	0.020	-0.794	0.01913	1	3.655	0.077
9	GLP*RAP	-0.041	0.016	-0.759	0.03992	1	6.961	0.019
10	GLP*GLP	0.079	0.019	1.277	0.03402	1	16.786	0.001
Out		Part. Corr.						
6	RAP*FAP	0.359	.	.	0.18563	1	1.929	0.188
7	GLP*FAP	0.111	.	.	0.03109	1	0.164	0.692
8	RAP*RAP	0.154	.	.	0.05493	1	0.316	0.583

Step # 4 R = 0.973 R-Square = 0.947
Term removed: GLP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	2.680	0.877	1.313	0.01908	1	9.333	0.008
3	RAP	1.182	0.169	0.701	0.34958	1	48.720	0.000
5	FAP*FAP	-0.035	0.021	-0.714	0.01949	1	2.822	0.114
9	GLP*RAP	-0.050	0.015	-0.918	0.04711	1	11.263	0.004
10	GLP*GLP	0.067	0.018	1.071	0.04341	1	14.136	0.002
Out		Part. Corr.						
4	GLP	-0.354	.	.	0.05010	1	2.006	0.178
6	RAP*FAP	0.344	.	.	0.18573	1	1.882	0.192
7	GLP*FAP	0.066	.	.	0.03145	1	0.062	0.808
8	RAP*RAP	0.219	.	.	0.05773	1	0.703	0.416

Step # 5 R = 0.968 R-Square = 0.937
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	Constant							
2	FAP	1.221	0.130	0.598	0.97025	1	88.426	0.000
3	RAP	1.324	0.155	0.785	0.46436	1	72.835	0.000
9	GLP*RAP	-0.065	0.013	-1.186	0.07130	1	25.530	0.000
10	GLP*GLP	0.088	0.013	1.407	0.08556	1	43.162	0.000
Out		Part. Corr.						
4	GLP	-0.268	.	.	0.05105	1	1.158	0.299
5	FAP*FAP	-0.398	.	.	0.01949	1	2.822	0.114
6	RAP*FAP	0.267	.	.	0.18827	1	1.156	0.299
7	GLP*FAP	0.187	.	.	0.03515	1	0.541	0.473
8	RAP*RAP	0.172	.	.	0.05802	1	0.459	0.508

Dep Var: TPD N: 21 Multiple R: 0.968 Squared multiple R: 0.937

Adjusted squared multiple R: 0.921 Standard error of estimate: 7.051

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	-13.182	4.330	0.000	.	-3.045	0.008
FAP	1.221	0.130	0.598	0.970	9.404	0.000
RAP	1.324	0.155	0.785	0.464	8.534	0.000
GLP*RAP	-0.065	0.013	-1.186	0.071	-5.053	0.000
GLP*GLP	0.088	0.013	1.407	0.086	6.570	0.000

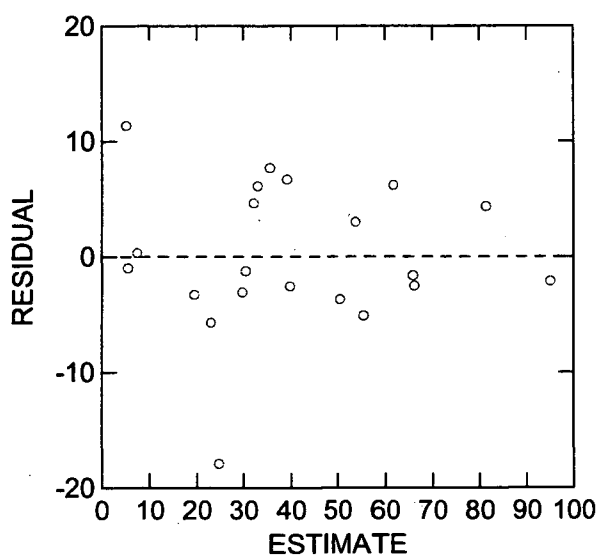
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	11865.522	4	2966.380	59.669	0.000
Residual	795.420	16	49.714		

*** WARNING ***
Case 3 has large leverage (Leverage = 0.587)
Case 19 has large leverage (Leverage = 0.647)
Case 20 is an outlier (Studentized Residual = -3.500)

Durbin-Watson D Statistic 2.475
First Order Autocorrelation -0.240

Plot of Residuals against Predicted Values



Step # 0 R = 0.995 R-Square = 0.989

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	2.573	1.001	0.947	0 .00652	1	6.600	0.025
2	RAP	0.543	0.321	0.406	0 .01538	1	2.862	0.116
3	GLP	-0.893	0.583	-0.323	0 .01989	1	2.343	0.152
	FAP*FAP				0			

4		-0.041	0.021	-0.505	.01250 0	1	3.601	0.082
5	RAP*FAP	0.011	0.008	0.139	.08602 0	1	1.889	0.194
6	GLP*FAP	0.001	0.039	0.007	.01618 0	1	0.001	0.977
7	RAP*RAP	0.005	0.005	0.168	.03366 0	1	1.073	0.321
8	GLP*RAP	-0.039	0.018	-0.535	.01390 0	1	4.491	0.056
9	GLP*GLP	0.078	0.031	0.805	.00857	1	6.269	0.028

Out		Part. Corr.
	none	

Dependent Variable TPD
Minimum tolerance for entry into model = 0.000000

Backward stepwise with Alpha-to-Enter=0.050 and Alpha-to-Remove=0.050
Step # 1 R = 0.995 R-Square = 0.989
Term removed: GLP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	2.588	0.809	0.953	0.00921	1	10.226	0.007
2	RAP	0.541	0.300	0.404	0.01625	1	3.250	0.095
3	GLP	-0.893	0.560	-0.323	0.01989	1	2.540	0.135
4	FAP*FAP	-0.041	0.019	-0.508	0.01403	1	4.423	0.056
5	RAP*FAP	0.011	0.007	0.141	0.11227	1	2.725	0.123
7	RAP*RAP	0.005	0.004	0.169	0.03450	1	1.201	0.293
8	GLP*RAP	-0.039	0.015	-0.539	0.01939	1	6.882	0.021
9	GLP*GLP	0.078	0.018	0.812	0.02286	1	18.448	0.001
Out		Part. Corr.						
6	GLP*FAP	0.008	.	.	0.01618	1	0.001	0.977

Step # 2 R = 0.994 R-Square = 0.988
Term removed: RAP*RAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	2.410	0.799	0.887	0.00959	1	9.108	0.009
2	RAP	0.816	0.166	0.609	0.05357	1	24.001	0.000
3	GLP	-1.255	0.456	-0.454	0.03041	1	7.552	0.016
4	FAP*FAP	-0.038	0.019	-0.469	0.01433	1	3.809	0.071
5	RAP*FAP	0.013	0.007	0.161	0.11777	1	3.684	0.076
8	GLP*RAP	-0.037	0.015	-0.502	0.01991	1	6.055	0.027
9	GLP*GLP	0.084	0.018	0.874	0.02511	1	23.155	0.000
Out		Part. Corr.						
6	GLP*FAP	0.053	.	.	0.01659	1	0.037	0.851
7	RAP*RAP	0.291	.	.	0.03450	1	1.201	0.293

Step # 3 R = 0.993 R-Square = 0.985
Term removed: RAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	2.452	0.867	0.903	0.00960	1	8.002	0.013
2	RAP	0.944	0.166	0.705	0.06389	1	32.523	0.000
3	GLP	-1.589	0.458	-0.575	0.03558	1	12.018	0.003
4	FAP*FAP	-0.030	0.021	-0.376	0.01495	1	2.157	0.163
8	GLP*RAP	-0.036	0.016	-0.494	0.01992	1	4.976	0.041
9	GLP*GLP	0.094	0.018	0.970	0.02715	1	26.133	0.000
Out		Part. Corr.						
5	RAP*FAP	0.456	.	.	0.11777	1	3.684	0.076
6	GLP*FAP	0.274	.	.	0.02243	1	1.133	0.305
7	RAP*RAP	0.351	.	.	0.03619	1	1.970	0.182

Step # 4 R = 0.992 R-Square = 0.983
Term removed: FAP*FAP

	Effect	Coefficient	Std Error	Std Coef	Tol.	df	F	'P'
In								
1	FAP	1.192	0.127	0.439	0.48157	1	88.411	0.000
2	RAP	1.123	0.116	0.839	0.13980	1	93.952	0.000
3	GLP	-1.276	0.420	-0.461	0.04540	1	9.221	0.008
8	GLP*RAP	-0.052	0.012	-0.713	0.03648	1	17.711	0.001
9	GLP*GLP	0.107	0.016	1.111	0.03654	1	43.052	0.000
Out		Part. Corr.						
4	FAP*FAP	-0.355	.	.	0.01495	1	2.157	0.163
5	RAP*FAP	0.346	.	.	0.12284	1	2.037	0.174
6	GLP*FAP	0.315	.	.	0.02316	1	1.651	0.218
7	RAP*RAP	0.256	.	.	0.03750	1	1.056	0.321

Model contains no constant

Dep Var: TPD N: 21 Multiple R: 0.992 Squared multiple R: 0.983

Adjusted squared multiple R: 0.979 Standard error of estimate: 7.058

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	1.192	0.127	0.439	0.482	9.403	0.000
RAP	1.123	0.116	0.839	0.140	9.693	0.000
GLP	-1.276	0.420	-0.461	0.045	-3.037	0.008
GLP*RAP	-0.052	0.012	-0.713	0.036	-4.208	0.001
GLP*GLP	0.107	0.016	1.111	0.037	6.561	0.000

Analysis of Variance

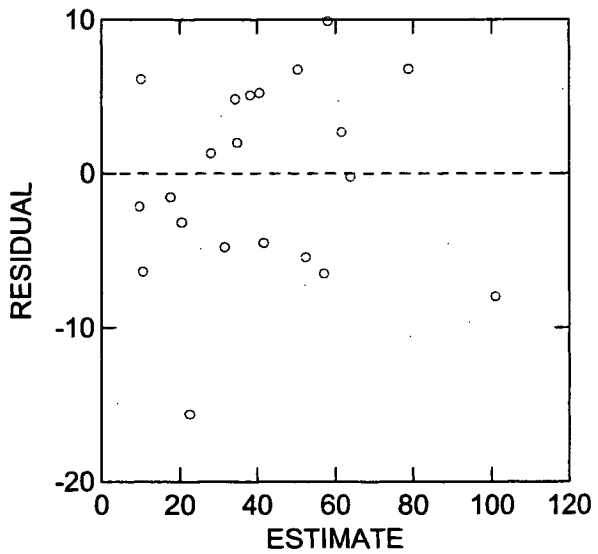
Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	46723.585	5	9344.717	187.611	0.000
Residual					

	796.945	16	49.809

*** WARNING ***
Case 3 has large leverage (Leverage = 0.775)
Case 3 is an outlier (Studentized Residual = -2.886)
Case 19 has large leverage (Leverage = 0.650)
Case 20 is an outlier (Studentized Residual = -2.897)

Durbin-Watson D Statistic 2.253
First Order Autocorrelation -0.157

Plot of Residuals against Predicted Values



Model contains no constant

Assuming Mixture Model

Dep Var: TPD N: 21 Multiple R: 0.968 Squared multiple R: 0.937

Adjusted squared multiple R: 0.921 Standard error of estimate: 7.058

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
FAP	1.192	0.127	0.850	0.482	9.403	0.000
RAP	1.123	0.116	1.626	0.140	9.693	0.000
GLP	-1.276	0.420	-0.894	0.045	-3.037	0.008
GLP*RAP	-0.052	0.012	-1.382	0.036	-4.208	0.001
GLP*GLP	0.107	0.016	2.153	0.037	6.561	0.000

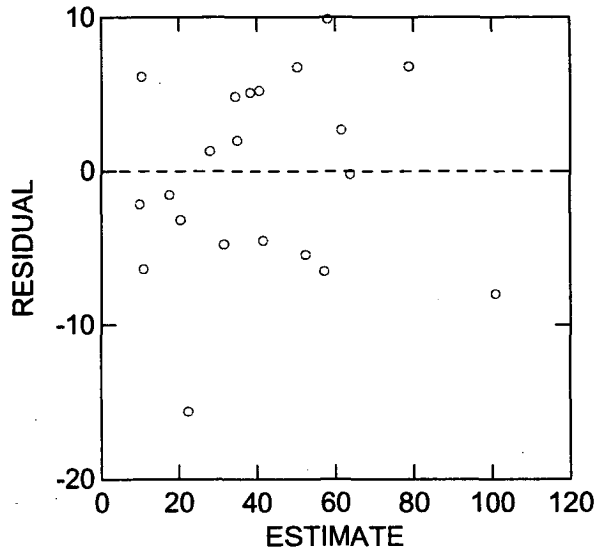
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	11863.996	4	2965.999	59.547	0.000
Residual	796.945	16	49.809		

*** WARNING ***
Case 3 has large leverage (Leverage = 0.775)
Case 3 is an outlier (Studentized Residual = -2.886)
Case 19 has large leverage (Leverage = 0.650)
Case 20 is an outlier (Studentized Residual = -2.897)

Durbin-Watson D Statistic 2.253
First Order Autocorrelation -0.157

Plot of Residuals against Predicted Values



Dep Var: TPD N: 21 Multiple R: 0.970 Squared multiple R: 0.942

Adjusted squared multiple R: 0.922 Standard error of estimate: 7.016

Effect	Coefficient	Std Error	Std Coef	Tolerance	t	P(2 Tail)
CONSTANT	-7.461	6.843	0.000	.	-1.090	0.293
FAP	1.223	0.129	0.599	0.970	9.464	0.000
RAP	1.255	0.167	0.744	0.397	7.515	0.000
GLP	-0.714	0.663	-0.297	0.051	-1.076	0.299
GLP*RAP	-0.059	0.014	-1.080	0.061	-4.266	0.001
GLP*GLP	0.100	0.018	1.606	0.049	5.698	0.000

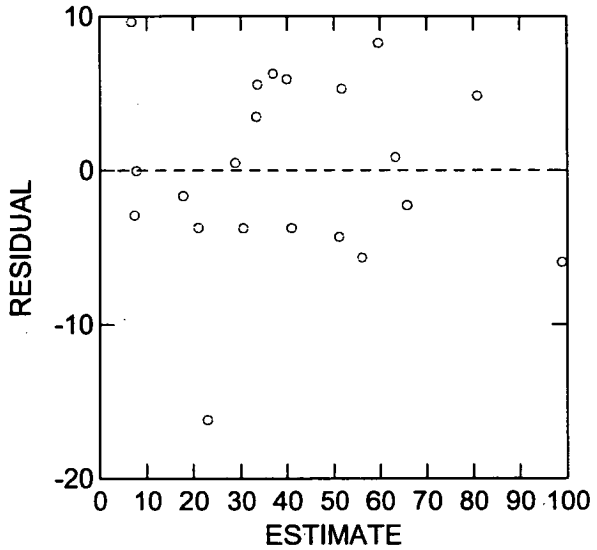
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Regression	11922.508	5	2384.502	48.437	0.000
Residual	738.433	15	49.229		

*** WARNING ***
Case 3 has large leverage (Leverage = 0.845)
Case 19 has large leverage (Leverage = 0.658)
Case 20 is an outlier (Studentized Residual = -3.185)

Durbin-Watson D Statistic 2.420
First Order Autocorrelation -0.216

Plot of Residuals against Predicted Values



APPENDIX G - PUBLICATIONS

1. McLean, D.S., Stack, K.R., and Richardson, D. Wood pitch deposition versus composition. in 57th Appita Annual General Conference Proceedings. 2003. Melbourne, Australia. p. 203-210

2. McLean, D., Stack, K., and Richardson, D. Wood pitch deposition versus composition. in WPP 2003 Chemical Technology of Wood, Pulp and Paper International Conference. 2003. Bratislava, Slovak Republic. p. Not Yet Published